PETROLEUM AND NATURAL-GAS RESEARCH PROGRAM, BUREAU OF MINES, FISCAL YEAR 1951

BY R. A. CATTELL AND OTHERS

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by

R. A. Catlell[1/] and others

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1/ Chief, Petroleum and Natural Gas Branch, Bureau of Mines, Washington, D. C.

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SUMMARY AND INTRODUCTION

The peacetime activities of the Bureau's petroleum and natural-gas program have been reoriented to serve the needs of a national-defense program. When the United Nations sent troops to Korea after the North Korean Army crossed the 38th parallel in the latter part of June 1950, the Bureau's coordinated national program on petroleum and natural gas, with each major project forming an essential member of its framework, was carefully reviewed by those in charge of the work. As a matter of fact, the era of normalcy in which the petroleum and natural-gas research of the Bureau of Mines prospered during the fiscal year 1950[2/] was no sedative to the need for alertness on a national-defense front. The program, although conducted along peacetime lines in general, was scanned critically and repeatedly during that period to see where - if the need should arise - the emphasis could be shifted from peace to defense or war. Judging from the experience of two wars, it would not be long before the Bureau would be asked to use its trained technical personnel in applying techniques already learned in peacetime research to the requirements of munition and fuel needs of national defense.

Near the end of January 1951, petroleum and natural-gas engineers of the Bureau of Mines began a comprehensive study of reservoir conditions in the Canyon Reef fields of Scurry, Borden, and Kent Counties, Tex. This work was preceded by published analyses of crude oils from Scurry County as early as April 1950. Well-informed persons in industry have estimated that these fields hold reserves that will yield 3 to 6 billion barrels of stock-tank oil. Although generally accepted good operating practices have been followed, engineering tests have shown that the natural energy, except in some favorable parts of the reservoir, will not be adequate for obtaining a high percentage of recovery. Correct information regarding the extent and availability of this vast reservoir of hydrocarbons is therefore of great concern to the Petroleum Administration for Defense in carrying out its responsibilities under the Defense Production Act.

The work in the Scurry County area is being conducted as a cooperative undertaking by the Bureau of Mines and the Geological Survey, United States Department of the Interior, reports being made directly to the Petroleum Administration for Defense. Tangible results were reported only 6 months after the study was begun, because of long-standing informal cooperation with industry and because experimental procedures based on experience gained during past years were utilized fully. This type of cooperation and planning has paid high dividends to all concerned throughout the 37 years in which the Bureau has been conducting research on petroleum and natural gas.

2/ Cattell, R. A., and others, Petroleum and Natural-Gas Research Program, Bureau of Mines, Fiscal Year 1950: Bureau of Mines Inf. Circ. 7616, 1951, 38 pp.

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Before actual field work was begun, representatives of the Bureau of Mines and the Geological Survey, guided by their experience in dealing with field problems of broad scope, developed a tentative program for review by operators, members of engineering committees, and other responsible officials in the petroleum industry. The final program incorporated the views of these industry specialists. It was evident from the beginning that duplication of effort should be kept to the minimum, both with respect to the geologic and engineering parts of the project and with respect to work already done by the companies. For these reasons the Bureau's organization of work teams has been kept as flexible as possible, and no attempt has been made to conduct a conventional field study of the whole area. Instead, the Bureau engineers have utilized all available information from the companies, the Railroad Commission of Texas, and other sources that would shed light on this massive carbonate reservoir. They have made field tests only when it was necessary to obtain additional or more exact information regarding interconnection of the reservoir spaces, the feasibility of stopping excessive pressure decline, or the quantitative magnitude of the reserves and their availability.

As described in more detail later, one progress report on pressure-build-up and well-interference tests in the Scurry Reef of the Kelly-Snyder area has been completed; and a second, giving much-needed information on the relatively small variations in the composition and physical properties of the oil in the Kelly-Snyder, Diamond M, and Sharon Ridge areas in Scurry County, was nearing completion as the fiscal year 1951 closed.

Oil-field cores from Scurry and adjacent counties were analyzed by the core laboratories at Bartlesville, Okla., which are maintained as part of the secondary-recovery group. The core-laboratory staff in Dallas cut samples of oil-field cores from Scurry County and shipped them to Bartlesville for analysis. The schedule that has been maintained in the laboratories has done much to advance the field work.

Another activity of the secondary-recovery group is the fundamental research on the nature of surface forces in petroleum reservoirs, which took a definite turn in the direction of applicability. One of the three major problems in this research project pertaining to retention of oil in reservoir rocks deals with film-forming substances. In earlier research, already reported, minute quantities of titanium, zinc, calcium, and magnesium were identified in the highly surface-active fractions of materials adsorbed at crude petroleum-water interfaces. The manifest interest in recent months in trace metals in crude petroleum has called attention to the likelihood of applying some of the knowledge gained in the fundamental work to important defense problems of not only identifying trace metals in crude petroleum but also of finding means of removing them.

The 1950 report referred to ground breaking for a new radiochemical laboratory at Bartlesville, Okla. This well-equipped working place has been completed and put into service, and initial work in the study of radioisotopes as tracers in water flooding and air and gas repressuring has begun in earnest. It is noteworthy that when completed the building was visited by a member of the Field Advisory Service, Isotopes Division, Atomic Energy Commission, Oak Ridge, Tenn. After inspecting the radiochemical laboratory and discussing personnel safeguards, controls, and tracer-study plans, he reported that he found the building and its facilities unexcelled by any other laboratory of its kind not directly connected with the Commission.

In laboratories at Franklin and Bradford, Pa., and College Park, Md., and in oil fields of the Appalachian region, technologists conducted comprehensive fundamental and applied research directed toward developing new or improved methods of operating stripper oil fields (depleted of their native oil-driving gas energy yet containing great quantities of petroleum) and designed to lower production costs and to increase ultimate recovery of oil. In the Appalachian region, where less than 20 percent of the stripper properties have been subjected to secondary-recovery methods

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and opportunity exists for new, deeper flush production, Bureau research is geared to encompass effectively both secondary-recovery and primary-recovery problems.

Engineering studies of selected oil fields, laboratory and field investigations of practical development and operational problems, and fundamental studies of the reservoir rocks and flow through them of contained fluids furnished new knowledge on how to keep in operation oil fields nearing minimum economic rates of production and how to rehabilitate them to secure maximum ultimate recovery.

The four-part study of Diesel fuels is outstanding because of its direct applicability to the defense program. In cooperation with the Western Petroleum Refiners Association, a long-time study was begun of the basic causes of the instability and incompatibility of distillate fuels, particularly in the Diesel-fuel range, thus establishing a well-balanced Diesel-fuels research program complementing and supporting the studies of the composition of Diesel fuels, which have been under way for a number of years. Concurrently with these studies has been development of a constant-volume combustion bomb and its accessories, fostered by the cooperation of the Coordinating Research Council, Inc. The bomb in its present state of development gives reproducible and accurate results and permits study of a wide range of temperature and pressure conditions as they affect the combustion of Diesel fuels; yet it utilizes only very small quantities - as little as 10 ml. - of fuel for this purpose. The Coordinating Research Council also is sponsoring some work on the composition of test fuels being used in full-scale railroad Diesel-engine tests, all of which dovetails with the Bureau's program. The fourth part of the Diesel-fuels program is the annual Diesel-fuel survey, first made in 1950. This activity is sponsored by the American Petroleum Institute under a cooperative agreement.

The broad aspects of the four major activities of the Diesel-fuels program and the fact that almost all of the work is being conducted under cooperative agreements with commercial organizations indicate the widespread interest in this work. This condition was attested by industry participation in the fifth annual Diesel-Fuel Conference at Bartlesville, Okla., in May 1951. The 2-day meeting was attended by 72 participating guests, who represented not only the refiners who manufacture the fuel but also engine builders, users of fuel in large quantities, and others, including Army and Navy personnel, who are interested in and concerned about Diesel-fuel performance and availability.

Another development of major interest during the year was the use of routine crude-oil analyses for estimating the content of "aromatics" and "paraffins plus naphthenes" in the distillates and of "naphthene rings" and "paraffins plus paraffin side chains" in the paraffin-naphthene portions of the distillates. This has been possible because of correlations determined over the last several years. These correlations show the relationships between the composition of fractions from the routine-type analysis and their simple physical properties. The development of such figures from a routine analysis represents an advance in the analysis of crude petroleum, as it permits a relatively good estimation of the characteristics of a crude oil from a comparatively inexpensive and quick analytical method. The description of the routine method for analyzing crude oil was published as a bulletin3/ to replace the one published about 30 years ago, which has been out of print for some time.

3/ Smith, N. A. C., Smith, H. M., Blade, O. C., and Garton, E. L., Routine Method for the Analysis of Crude Petroleum. I. The Analytical Method: Bureau of Mines Bull. 490, 1951, 82 pp.

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In the report for 1950, the study of sulfur compounds in crude oil under the sponsorship of American Petroleum Institute Research Project 48A was cited as an excellent sample of a fundamental approach, with the cooperative aid of industry, to the solution of a problem that is almost as old as the industry. During 1951 all sulfur compounds theoretically possible, except thiophene, were identified in a distillate boiling up to about 95° C., prepared from Wasson, Tex., crude oil. Three sulfur compounds not heretofore identified in crude oil were found. In conjunction with this finding, several pure-sulfur compounds were prepared and their important properties determined. These compounds are being used to develop new analytical methods and for determining their thermodynamic properties. These and other results discussed later are evidence of continuing dividends from this cooperative work.

Many large-scale processes in the rapidly growing chemical industry have been aided greatly by the application of thermodynamic knowledge. The science of thermodynamics, although unspectacular in its outward aspects, has, nevertheless, played an extremely important role in the manufacture of ammonia for explosives and fertilizers, in the manufacture of synthetic rubber, in the production of toluene and benzene for explosives, and in the large-scale production of special "tailored" fuels for aviation. Thermodynamic data also have found application in the processing of "superfuels" for the most-modern types of flight propulsion and for use in recently developed long-range submarines.

Recognizing this increasing dependence upon thermodynamic data, the staff at Bartlesville, Okla., engaged in this work, has as its primary objective attainment of results having the utmost reliability. By these means, chemists and chemical engineers throughout the country will be aided most in their efforts to improve old and to devise new processes. As a byproduct of this work, fundamental scientific information is being added to man's store of knowledge, and this will have enduring value. During the past 12 months, significant progress has been made along the charted path. Valuable information has been obtained and released to those who can use it most effectively by publication in well-known scientific journals and through official reports of the American Petroleum Institute. Of outstanding international interest is the final achievement of experimental methods that will provide accurate values of the heats of combustion of highly corrosive sulfur compounds. A description of these techniques has been prepared for the Commission on Thermochemistry of the International Union of Pure and Applied Chemistry.

The reported thermodynamic properties of a relatively large number of corrosive sulfur compounds as an integral and important part of American Petroleum Institute Research Project 48A are discussed in the main part of this report under appropriate captions pertaining to the Bureau's work on thermodynamics of petroleum.

Along with the increased tempo of defense activities there has been one minor note of importance, the true significance of which may not be felt for years to come. It has been demonstrated that the language of science recognizes no national boundaries, and probably no other single activity in the petroleum and natural-gas work of the Bureau of Mines has done as much to establish good will in various parts of the world as the exchange of visits, permitting an exchange of ideas, with scientists of foreign countries. Many have visited the several research centers of the Bureau. In turn, the benefits derived by representatives of the Bureau of Mines in visits to foreign countries are many fold. During the year the Petroleum Experiment Station at Bartlesville was host to over 20 foreign scientists and technologists. Sponsorship for these visitors comes from such organizations as the Economic Cooperation Administration (now the Mutual Security Agency), the Scandinavian-American Foundation (an organization dedicated to improving relations between Scandinavian

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and United States scientists), the Interdepartmental Committee on Scientific and Cultural Cooperation (which provides means for nationals of South American countries to participate in training grants in this country), and General Headquarters, Supreme Commander for Allied Powers, Natural Resources Section, in Tokyo. Countries represented by these visitors are Venezuela, Iran, France, Italy, Egypt, Mexico, Canada, Japan, Sweden, Denmark, the Netherlands, Uruguay, and England. The visiting scientists and their hosts in the Bureau of Mines - particularly members of its staff who have traveled abroad - feel that there is no better way of creating friendly relations between nations than by exchanging ideas in the scientific field. Invariably, discussions of the humanities that affect all peoples follow, and better international understanding is established.

The petroleum and natural-gas program of the Bureau of Mines is discussed under the following general captions: Oil and Gas Development and Production, Secondary Recovery, Chemistry and Refining, Thermodynamics of Petroleum, Transportation of Natural Gas, and Helium-Tracer Studies.

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assistance under 16 cooperative agreements. The Bureau is extremely grateful for this valuable help and expresses appreciation to the following cooperators: State of Oklahoma, Kansas State Board of Health, Arkansas Oil and Gas Commission, University of Wyoming, Texas Technological College, American Petroleum Institute, Natural Gas Department of American Gas Association, Coordinating Research Council, Inc., Pennsylvania Grade Crude Oil Association, North Texas Oil and Gas Association, American Society for Testing Materials, and Western Petroleum Refiners Association.

OIL AND GAS DEVELOPMENT AND PRODUCTION

Every resource was marshaled to meet the requirements of a comprehensive study of the oil-producing possibilities of the Canyon Reef fields of Scurry, Borden, and Kent Counties, Tex. The work was begun in January 1951 as a cooperative geologic and engineering undertaking pursuant to an agreement between the Bureau of Mines and the Geological Survey, United States Department of the Interior, and the Petroleum Administration for Defense. Not only have petroleum engineers of the Bureau, with headquarters at Dallas, Tex., and Bartlesville, Okla., combined forces to initiate the engineering studies in the fields of the area, but those engaged in special reservoir studies pertaining to such subjects as productivity of high-pressure oil and gas wells and reservoir oil samples have directed their researches to the problems of this important area. Also, the facilities of the core laboratories of the two headquarters were augmented to handle the large number of cores to be analyzed. In the appropriate sections that follow specific reference is made to the work of each group relating to this defense measure.

Petroleum-Engineering Studies

Canyon Reef Fields in Scurry, Borden, and Kent Counties, Tex.

The purpose of this study is to supply information that will aid the Petroleum Administration for Defense in meeting its responsibilities under the Defense Production Act. In addition, assistance in exploration, development, and operation is being given to the producers by furnishing them with impartial engineering data on a field-wide basis. Naturally, the work of the Bureau will follow the long-established pattern of its engineering field reports, and close attention will be given to estimates of the reserves and the availability of oil and gas from the Canyon Reef fields. The fields covered by this study have about 1,800 wells extending over an area approximately 50 miles long and 6 miles wide. The reserves of this section will play an important part in national defense, as they have been estimated variously by technologists in industry as ranging from 3 to 6 billion barrels of stock-tank oil. The wells in these fields have not been producing at rates that normally would be considered excessive. However, engineering tests have disclosed that the natural energy, except in some favorable parts of the reservoir, will not be enough to obtain a high percentage of recovery, and petroleum technologists have diversified opinions as to the benefits that might be realized by supplementing the natural reservoir energy. Bureau engineers are giving close attention to this problem.

At the end of fiscal year 1951, three work teams were in the field collecting and analyzing production data. Individual well records for approximately 600 wells, one-third of the total, had been completed from data on file in the offices of the Texas Railroad Commission, checked with and supplemented by company records. The objective is to obtain all information on wells that can be used for the specific purposes of the study. A list of nearly 200 known cored wells in the area had been prepared for use in obtaining core analyses from the operators. Analyses of over half of this number had been obtained for study in addition to the cores actually sampled (plugged) and analyzed by the Bureau of Mines, as discussed in a subsequent section of this report.

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Conditions in the reservoir may also be analyzed by means of electric and radioactive logs. Over 600 logs of various types suitable for quantitative interpretations have been collected and studied to aid in the increased usefulness and accuracy of the reservoir analysis. Production data are being kept current on a cumulative basis, and a preliminary report will be made to the Petroleum Administration for Defense as soon as the findings of the field study warrant.

Big Lake Field, Tex.

Writing of the final report giving a petroleum-engineering analysis of the Ellenburger reservoir in the Big Lake field, Reagan County, Tex., had to be postponed to meet the requirements of the special work for the Petroleum Administration for Defense discussed in the preceding section. The Ellenburger reservoir in this field was discovered in 1928 and is approaching commercial depletion, after producing over 30 million barrels of oil.

Productivity of High-Pressure Oil and Gas Wells

Accurate subsurface-pressure measurements are especially important in research being conducted by Bureau of Mines engineers on the productivity of high-pressure oil and gas wells. Accordingly, an intensive study of subsurface-pressure gages was completed, and the results - giving the calibration characteristics and improved methods of using the gages - were published.4/

This paper presents the calibration characteristics of seven Amerada-type subsurface-pressure gages, with upper pressure limits ranging from 700 to 7,000 pounds per square inch. In addition, the curvature characteristics and hysteresis effects found by this study are given. The principle of operation of the gage is such that deflections resulting from the action of pressure are recorded on a chart, and the measured deflections may be converted to pressure by means of the gage modulus, the zero-pressure correction, and the curvature correction for the gage. When the pressure is increased to a maximum for the particular range of a gage and then decreased to a pressure less than the maximum, a fourth characteristic, hysteresis, also influences the deflection. The modulus, zero-pressure correction, and curvature correction are determined readily by calibration. Hysteresis effects depend upon the immediate past pressure treatment of the gage, and, although their magnitude may be determined by special calibrations, conditions that produce hysteresis effects should be avoided.

The field investigation of friction factors for flow in gas wells was completed with determination of data for three gas wells equipped with 3-inch tubing. In addition, data have been developed from testing one well equipped with 1-1/4-inch tubing, two wells with 2-inch tubing, three wells with 2-1/2-inch tubing, three untubed wells with 5-1/2-inch casing, three wells with 7-inch casing, and the annular spaces between the tubing and casing of four wells. The friction factors for the various flow strings were correlated using the Colebrook equation, which relates friction factors to the relative roughness of the inner surface of the pipe and to Reynolds numbers, a measure of the similarity of flow. The results of this method of correlation indicated that a majority of the wells studied have absolute roughness values that are in close agreement. The data on friction factors permit accurate calculation of pressures at the sand face in flowing gas wells, providing a sound basis for evaluating the productivity of gas wells.

4/ Smith, R. V., Dewees, E. J., and Williams, R. H., Calibration Characteristics of Subsurface-Pressure Gages: Petrol. Eng., Drilling and Producing Ed., vol. 23, January 1951, pp. B 7-12.

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Pressure Build-up and Well-Interference Tests, Scurry County, Tex.

When the defense work in the Canyon Reef fields came to the forefront, it soon became evident that the Bureau's earlier study of the productivity of high-pressure oil and gas wells had provided a valuable experience factor in coping with the immediate problem. Accordingly, pressure build-up and interference tests were conducted on a well in the Kelly-Snyder area, Scurry County, Tex., to determine the effective permeability of the reservoir formation and the suitability of the reservoir for pressure maintenance by the injection of water or gas. The results of the tests gave the effective permeability of the reservoir formation to oil and the over-all permeability, including the effect on permeability of well-completion procedure. They also indicated that no highly permeable channels exist between the test well and off-set wells and that the reservoir within the test area is interconnected. On the basis of these field tests, reservoir conditions are favorable for gas or water injection to maintain reservoir pressure and increase the recovery of oil. These findings, with supporting data, were made available to the Petroleum Administration for Defense. Figure 1 shows field equipment, including a mobile test unit, used to obtain gas-oil ratio measurements in the Kelly-Snyder area.

Study of Reservoir-Oil Samples

Elk Basin field, Wyo. and Mont., and Rangely field, Colo.

The characteristics of the oil in a reservoir have an important bearing on the operations used for recovering oil from the reservoir. The oil in the Tensleep sandstone in the Elk Basin field, Wyo. and Mont., was studied to develop engineering facts that would aid in recovering as much oil as possible from this large reserve. Data developed indicated that the oil had unusually varying physical characteristics; for example, all the oil in the reservoir was undersaturated with gas, and the oil had a saturation pressure of 1,250 p.s.i.a., with 490 cubic feet of gas in solution in a barrel of oil at the crest of the structure; yet there was a saturation pressure of 530 p.s.i.a. and 134 cubic feet of gas in solution in a barrel of oil low on the flanks. Further, the hydrogen sulfide content of the gas in solution in the oil ranged from 18 percent for oil at the crest to 5 percent for oil low on the flanks of the structure. Moreover, these and other related characteristics varied according to the position of the oil in the structure.

The reservoir oil in the Weber sandstone in the Rangely field, Colo., was studied to develop information that could be used in recovering as much oil as possible, since, because of its size, a 1-percent increase in recovery represented 20 million barrels of oil. Data that were developed indicated that this oil also had varying physical characteristics. The reservoir has a gas cap, and some of the oil was saturated with gas. The oil had a saturation pressure of 2,560 p.s.i.a. with 440 cubic feet of gas in solution per barrel of oil at or near the gas cap, while a saturation pressure of 1,960 p.s.i.a. and 230 cubic feet of gas in solution per barrel of oil existed at the oil-water contact on the flanks. The presence of nitrogen in the solution gas of the oil in appreciable and varying amounts over the structure revealed the possible effects of nonhydrocarbon gases on the characteristics of the reservoir oil. These and related characteristics varied according to the position of the oil in the structure.

These findings are significant contributions to basic engineering knowledge of petroleum reservoirs. Many engineers and geologists believed that all the oil in a petroleum reservoir had rather uniform physical characteristics and that equilibrium conditions between the oil and gas prevailed in all underground accumulations. This

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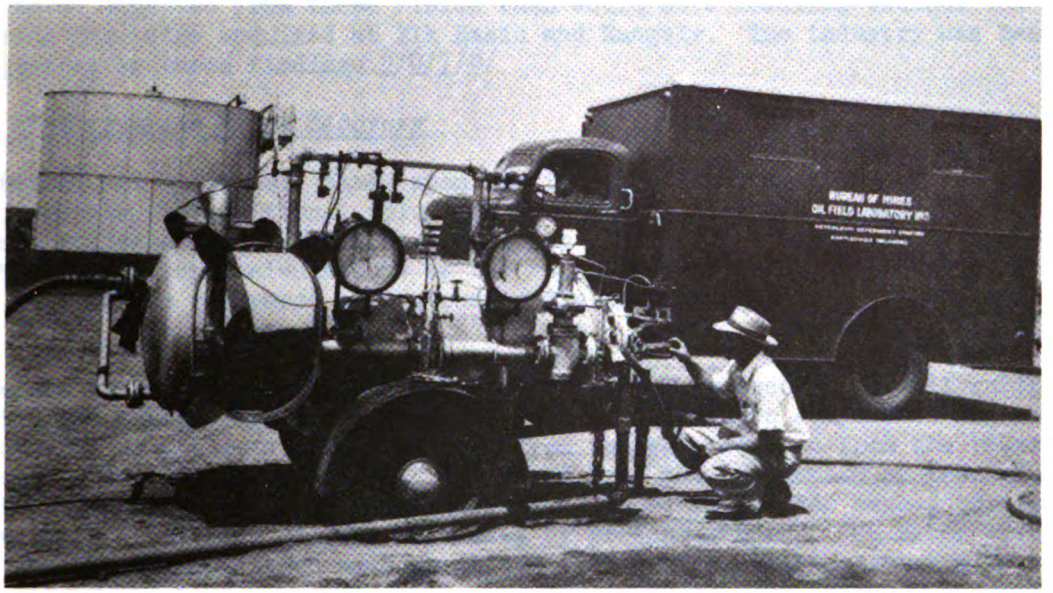

Figure 1. - Mobile unit used to obtain gas-oil ratio measurements in Kelly-Snyder area, Scurry County, Tex.

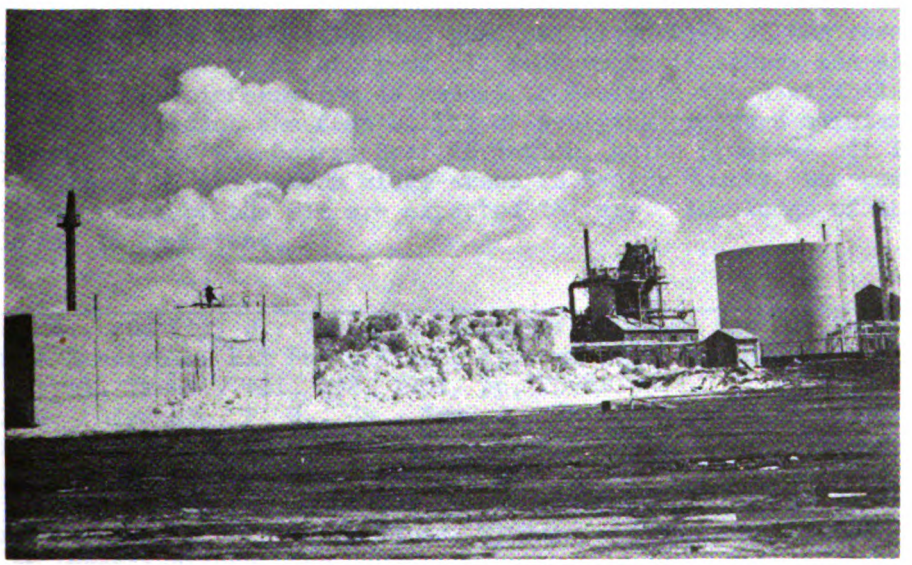

Figure 2. - Elk Basin, Wyo., sulfur stock pile, 30 tons daily production.

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concept can be erroneous and can lead to poor production programs. A greater yield of oil can be expected from these fields than would have resulted without the basic engineering knowledge acquired at Elk Basin and Rangely. The industry has been fully apprised of these findings.5/6/7/8/

Methods of Estimating Fluid Recovery

A method was developed, based upon special laboratory analyses of reservoir oil samples, whereby the additional volume of hydrocarbon liquid that will be recovered at various stages of depletion from a solution-gas-drive reservoir is recognized.9/ The method also allows calculations of the volume and composition of the hydrocarbon liquids that can be recovered by processing the produced gas in a natural-gasoline plant.

Present methods of estimating oil recoveries and production gas-oil ratios from reservoirs containing highly volatile oil need refinement to compensate for condensate recovered as a liquid stock-tank oil from the gas produced from the reservoir. The volume of the hydrocarbon liquid condensed from the production of the solution gas that has been liberated in some reservoirs may equal or even exceed the volume of recoverable stock-tank oil, as estimated by present methods. In other words, estimates made by commonly used methods of the recoverable oil from reservoirs containing oil of the highly volatile type may err by 50 to more than 100 percent because these methods of estimation do not include consideration of the liquid oil condensed from the solution gas. These methods include the false assumption that all of the free or liberated gas that enters the well bore remains in the gaseous phase as it is produced.

Variations in Composition of Oil, Scurry County, Tex.

Determination of the composition and physical properties of the reservoir oil is a part of the Bureau of Mines study of oil reservoirs in Scurry and adjacent counties of Texas. This information is needed to estimate the availability and reserves of oil and to predict the feasibility of applying pressure maintenance. Because of the magnitude of the Scurry Reef formation, which produces oil in the Kelly-Snyder, Diamond M, and Sharon Ridge areas in Scurry County, the composition and physical properties of the oil are expected to vary. Knowledge of the extent of this variation is important.

5/ Espach, R. H., and Fry, J., Variable Characteristics of the Oil in the Tensleep Sandstone Reservoir, Elk Basin Field, Wyo. and Mont.: Am. Inst. Min. and Met. Eng., Petrol. Trans., vol. 192, 1951, pp. 75-82.

6/ Cupps, C. Q., Lipstate, P. H., Jr., Fry, J., Variance in Characteristics of the Oil in the Weber Sandstone Reservoir, Rangely Field, Colo.: Bureau of Mines Rept. of Investigations 4761, 1951, 68 pp.

7/ Espach, R. H., and Fry, J., Variable Characteristics of the Oil in the Tensleep Sandstone Reservoir, Elk Basin Field, Wyoming and Montana: Bureau of Mines Rept. of Investigations 4768, 1951, 24 pp.

8/ Espach, R. H., Unusual Reservoir Oils in the Elk Basin and Rangely Fields: Presented at Am. Petrol. Inst., Div. of Production, Casper, Wyo., Apr. 20, 1951.

9/ Cook, Alton B., Spencer, G. B., and Bobrowski, F. P., Special Considerations in Predicting Reservoir Performance of Highly Volatile Type Oil Reservoirs: Am. Inst. Min. and Met. Eng., Jour. Petrol. Technol., vol. III, No. 2, February 1951, pp. 37-46.

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Extensive reservoir-oil sampling to determine variations in the properties of the oil being impractical, alternate procedures were adopted whereby it was first determined if wide variations could be expected by conducting a survey of the gravity of the oil produced throughout the field under controlled conditions. This survey is being followed by precise gas-oil-ratio tests of approximately 50 key wells, reservoir oil samples to be taken from 6 to 8 wells. The properties of the oil, as determined by analyses of the reservoir samples, will be correlated with the gas-oil ratio data and applied to the entire reservoir.

The survey of the gravity of the oil produced under controlled conditions indicates that only minor variations in the physical properties of the oil are to be expected, and this information has been made available to the Petroleum Administration for Defense.

Evaporation of Reservoir Oil by Cycling Gas

A laboratory model of an oil reservoir has been built to determine the extent to which cycling dry natural gas through an oil reservoir in a pressure-maintenance project will evaporate the oil. Pressure maintenance is applied by injecting natural gas or water into the oil reservoir. This injection results in the hydrocarbon fluid remaining in its original physical state (liquid or gas) if the initial pressure is maintained. The injected fluid drives the oil to the producing wells and may result in increased oil recovery amounting to two or three times that expected through normal production. Experience and theoretical considerations indicate that, when a dry gas passes through an oil reservoir, part of the oil evaporates and is produced in association with that gas. Laboratory data are needed for planning field tests whereby the greatest ultimate recovery of oil is obtained with pressure maintenance, or some modification of present methods.

Characteristics of Gas-Condensate Fluids

The manuscript for the monograph, Phase Relations of Gas-Condensate Fluids, now includes 340 illustrations and tables, and substantial progress has been made on the research that has been necessary to determine the best methods for correlating all the original data. Several correlations have been prepared or determined to be feasible pertaining to the liquid-gas ratio of fluids at given temperatures and pressures. One of them will permit computation of approximate liquid-gas ratios of gas-condensate fluids with no more test information than the routine analysis of liquid from the stock tank. Correlations suited to a variety of operating conditions in the field are available, and the most accurate of these will require a single liquid-gas ratio measurement using a high-pressure separator at the well with subsequent low temperature-distillation analyses of liquid and gas samples taken from the separator.

Preparation of the manuscript has involved more than compiling for publication the experimental data obtained by the Bureau of Mines. Numerous research papers of other laboratories, published in the last 15 years, contain many data relating to simple mixtures that have been helpful in interpreting the behavior of complex gas-condensate fluids. Substantial use has been made of published data relating to the phase-boundary pressures of 18 two-component hydrocarbon systems in determining the relationship between cricondenbar pressure (maximum pressure for coexistence of gas and liquid phases) and normal boiling point of the components. The relationship provides a means for estimating phase-boundary pressures of mixtures of hydrocarbons as a function of composition of the components, and the data are being applied to gas-condensate fluids with indications that the phase diagram for a fluid can be estimated with knowledge of only the composition of the fluid.

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It has been found that critical pressures and temperatures of two-component hydrocarbon mixtures can be correlated in much the same way that cricondenbar pressures and temperatures were correlated. Investigations are in progress to determine whether the same concepts will be reliable for estimating the critical temperature and pressure of gas-condensate fluids. Such information would be helpful as a guide in determining whether some reservoirs of fluid should be produced as condensate reservoirs or as oil reservoirs.

The monograph will contain many original data pertinent to the conservation of hydrocarbons that can be obtained accurately only with special equipment like that constructed by the Bureau of Mines. Knowledge of the phase state of the hydrocarbon fluids, in high-pressure reservoirs particularly, is important if loss of liquid phase during the production process is to be kept at the minimum. These essential data obtained with the special equipment are being correlated in such a way that they may be applied to reservoir problems with simple test information, obtained with standard equipment, as the guide. In accomplishing this end, it has been helpful to draw freely upon published information relating to simple hydrocarbon systems that have had, for the most part, only academic interest.

Corrosion in Gas-Condensate Wells

Results of a part of the work of finding means for controlling corrosion in gas-condensate wells were published10/ in cooperation with the American Gas Association and the National Association of Corrosion Engineers. Thirty-four steels, alloyed or plated with chromium, nickel, copper, and aluminum, were compared as to corrosion resistance with steels commonly used in the manufacture of equipment for high-pressure wells. The laboratory test results obtained by the Bureau of Mines were substantiated later by results obtained in more elaborate and expensive tests made at wells in the field by a committee of association members; in addition, the laboratory tests provided information on possible bimetallic forms of corrosion that was not available elsewhere.

Removal of Liquid from Gas and Gas-Condensate Wells

Early in fiscal year 1951, a study was begun of the problem of removing liquids (water or hydrocarbons) from gas and gas-condensate wells. The first objective is to improve efficiency in flowing water from relatively shallow gas wells. The customary procedure in removing water from such wells is to "blow" the well through the tubing or casing to the atmosphere at periodic intervals.

Tests by Bureau engineers in the Hugoton gas field, Oklahoma Panhandle, indicated that many operators are unaware of the waste of natural gas caused by blowing wells to the atmosphere to remove water. A particular well, equipped with tubing and an automatic valve control for flowing the water production to an open pit, showed that flow periods could be reduced approximately 50 percent without affecting the allowable rate of production of the well. The saving in gas otherwise wasted would amount to approximately 66,000 cubic feet a day; economically this saving would amount to over $1,900 a year, natural gas being worth 8 cents per M cubic feet.

10/ Eilerts, C. K., Greene, Faye, Archer, F. G., Burman, L. M., and Good, Colleen, Laboratory Determination of Relative Corrosion Resistance of Metals Considered for Gas-Condensate Well Service: Sec. III - C Nat. Assoc. Corrosion Eng. Pub. 50-3, 1950.

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Field tests were conducted on gas wells of varying capacities and volumes of water production to determine minimum flow velocities of gas through tubing for producing specific volumes of water. Before enough material for a published report could be gathered, the work was suspended to permit the assigned personnel to give full time to defense assignments.

Well-Spacing Studies

During the years since World War II, oil-reservoir engineering research has become increasingly quantitative; and, more than ever before, its branches have become specialized provinces of scientific endeavor. In particular, fundamental studies of the behavior of oil-reservoir fluids (gas, oil, and water) in porous oil-productive rocks have been emphasized. The significance and the usefulness of the results of these studies in predictions of the performances of oil fields under various operating conditions are recognized by petroleum engineers generally. Not so well recognized or so well understood, however, is the direct bearing of reservoir fluid-flow research on the practical problem of spacing oil and gas wells in an optimum manner.

For many years Bureau engineers have considered that any acceptable solution to the well-spacing problem would be largely qualitative at best. These engineers reasoned that, if empirical analyses of oil-field data would not result in incontrovertible charts showing average well-spacing intervals (distances between wells) as functions of economic ultimate oil recovery for different reservoirs and reservoir conditions, a fundamental theoretical investigation should be the logical recourse. In this spirit, a comprehensive theoretical study of the well-spacing problem has been undertaken in the Bureau.

The empirical approach to the problem has not been abandoned, however, but merely set aside temporarily. It is hoped that the current theoretical work will uncover information that will make interpretation of field data easier and more fruitful in regard to the well-spacing problem.

The theoretical study is well under way. The major objectives are to show the bearing of multiphase flow theory on the spacing of oil and gas wells and to expose the fundamental scientific nature of the problem as a whole. Accomplishment of these objectives should eliminate the present controversy over the nature of the problem, point the way to appropriate laboratory experimentation, and eventually lead to well-spacing - oil-recovery relationships that may be applied to oil-reservoir performance problems.

Drilling-Fluid Research

During the year, the Bureau's drilling-fluid research program has been directed to determining the behavior of different drilling fluids and the effects of their filtrates on core analysis and on the productivity of wells. In August 1950 the results[11] of analysis of cores obtained from wells in South Coles Levee, Calif., and Rangely, Colo., fields in the presence of oil-base drilling fluids containing an oil-soluble tracer were released. Earlier these data were submitted to the Special Study Committee on Well Spacing and Allocation of Production of the American Petroleum Institute, which cooperated on the problem by furnishing partial financial support.

11/ Gates, George L., Morris, Frank C., and Caraway, W. Hodge, Effect of Oil-Base Drilling-Fluid Filtrate on an Analysis of Cores from South Coles Levee, Calif., and Rangely, Colo., Fields: Bureau of Mines Rept. of Investigations 4716, 1950, 25 pp.

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The report describes use of a tracer in the oil-base drilling fluids to identify positively the quantity of their filtrates that entered the core samples. A proved satisfactory method of tracer analysis for determining the quantity of tracer in the filtrates is presented also.

Most cores that were analyzed in the laboratory contained filtrate from the oil-base drilling fluid that altered the oil content of the cores but did not affect the water content. The results and conclusions are based on more than 1,400 individual laboratory analyses of 125 core samples and 35 drilling-fluid samples. The report includes 19 figures that show the correlation of data obtained from individual core samples.

A corollary to the study of the effect of drilling-fluid filtrates on core analyses is the study of the effect of these filtrates resulting from their invasion into the oil-bearing formation during well completion on the permeability to oil of reservoir rocks. The effect of these filtrates is reflected in the productivity of the wells. An apparatus has been developed for determining the oil permeability of laboratory-saturated cores before and after they have been contaminated with drilling fluids and their filtrates. To date over 700 determinations of permeability to oil have been made on 21 core samples before and after they were subjected to invasion by filtrates from different types of water-base drilling fluids. In nearly all instances, the permeability to oil of the core samples was reduced by the filtrates. After several hours of reverse flow it was possible, only in a few tests, to restore the original permeability to oil of the sample. Filtrates having treating chemicals in solution were found to have a marked influence in reducing the permeability to oil of the specimens. The study has indicated that none of the clay-water muds tested have the desirable qualities required for completing oil wells with minimum reduction of permeability of the formation immediately surrounding the well. The ultimate objective of the study is to determine how water-base drilling fluids can be prepared having filtrates that will cause minimum resistance to the flow of oil and gas into well bores.

In recent years, several methods have been proposed for determining the water content of cores based on capillary phenomena as a measure of the water saturation of petroleum-reservoir rocks. These methods differ widely in technique, and a study has been begun to correlate the results obtained by the methods most frequently used. Three of the commonest of these methods are: (1) Displacement of interstitial water by air; (2) displacement of air by mercury; and (3) evaporation of liquid from the pore space.

The water saturations obtained by these three methods will be correlated with those obtained from core analysis of oil-base cores to evaluate the reliability of the new methods in relation to the analysis of cores cut in oil-base mud. The results of the study previously described indicate that the water content of cores cut with oil-base mud in the hole is a close approximation of the water saturation of the reservoir.

Nearing completion is a joint report of the Bureau of Mines and the California Division of Mines on the subject of San Benito County, Calif., clays and their prospective commercial use in oil-well drilling fluids and other products. The University of California and the Federal Geological Survey also have collaborated in the study by furnishing analytical data on the properties of the clays.

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Sulfur Recovery

The present potential for sulfur production in Wyoming was estimated to be 500 tons a day for the next 25 years. This was disclosed after a study of the reserves and availability of hydrogen sulfide gas produced with petroleum from numerous oil fields in the State[12/] was completed. The photographs (figs. 2 and 3) show the sulfur blocks at the two plants operating in Wyoming, where 330 tons a day is produced.

SECONDARY RECOVERY

The ever-increasing need for petroleum reemphasizes the fact that oil in the ground that is unrecoverable by known production methods is not yet a part of the Nation's petroleum reserves. Means of obtaining some part of the "remaining barrel of oil for every one produced" is a challenge to imaginative thinking and action. To that end, Bureau of Mines engineers are working closely with those in industry in all parts of the country: (1) To learn more about reservoir conditions through studies of fields now in their declining life; (2) to apply special techniques in solving field problems; and (3) through both fundamental and applied research in laboratories, to explore the vague and secret characteristics and behavior of reservoir rocks and their contained fluids. With increased knowledge from such cooperative effort with industry, the reserves attributable to stimulative methods applied to partly depleted fields should be increased greatly.

Field Studies

Washington County, Okla.

For the second successive year Bureau of Mines engineers arranged a tour of successful water-flooding projects to stimulate interest in application of secondary-recovery production methods and to permit operators of water-flooding projects to compare the results obtained by the use of different techniques and types of equipment. The tour, made by nearly 400 oil producers, engineers, and others interested in water flooding, included 5 projects in Washington County, Okla. A report[13/] describing water-flooding projects in the county, released at the time of the tour, added materially to the benefits obtained by the group. Figure 4 shows a part of the group as the report was being distributed preceding the field trip.

Washington County, Okla., has shown unusual activity in water flooding during the past few years. In 1942, 35 barrels of oil daily was produced from two water-flooding projects consisting of 90 developed acres. In March 1951, 4,000 barrels of oil was being produced daily by the injection of 58,000 barrels of water on 19 active projects covering 1,645 acres. Permits to water-flood over 8,000 acres in Washington County have been granted by the Oklahoma Corporation Commission. The county's yearly oil production increased from 1,076,000 barrels in 1948 to 1,720,000 barrels in 1950, principally as the result of water flooding. The effects of gas injection and water flooding on the oil-production history of the county are shown graphically in figure 5.

12/ Espach, R. H., Sources of Hydrogen Sulfide in Wyoming: Ind. Eng. Chem., vol. 42, 1950, pp. 2235-2237.

13/ Riggs, C. H., and Smith, William C., Water Flooding of Oil Sands in Washington County, Okla.: Bureau of Mines Rept. of Investigations 4795, 1951, 16 pp.; also Oil and Gas Jour. (published in 5 parts), part I, vol. 50, No. 4, May 31, 1951, pp. 117-118; part II, vol. 50, No. 5, June 7, 1951, pp. 88-89; part III, vol. 50, No. 6, June 14, 1951, pp. 103-104; part IV, vol. 50, No. 8, June 28, 1951, pp. 78-79; part V, vol. 50, No. 9, July 5, 1951, pp. 78-79.

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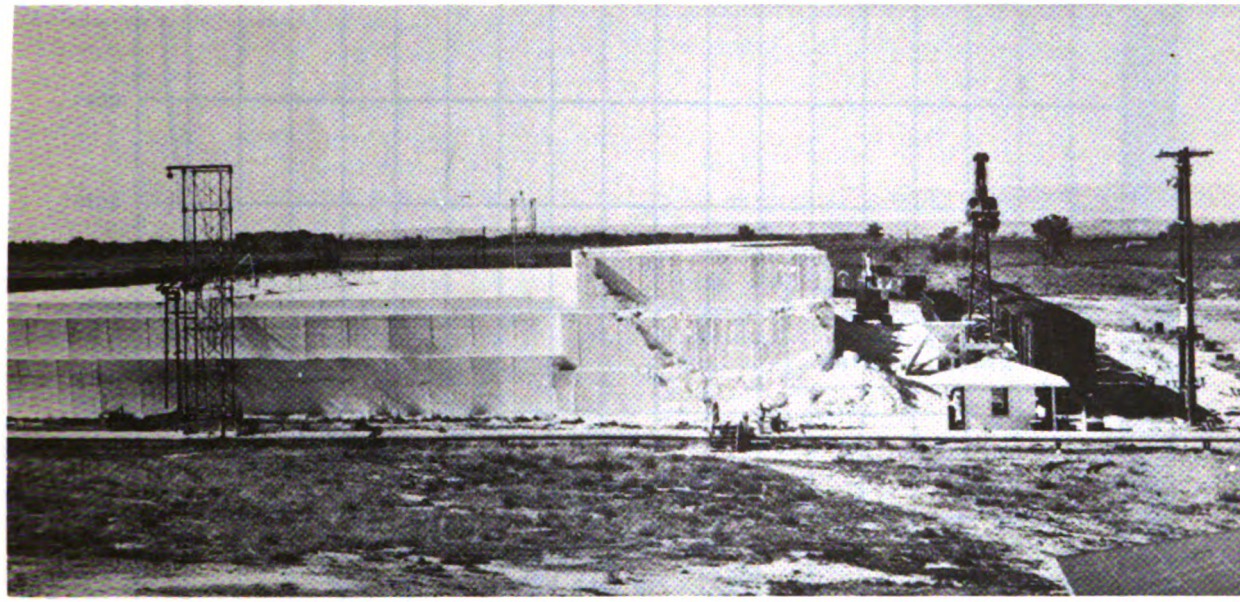

(Picture courtesy Texas Gulf Sulphur Co.)

Figure 3. - Elemental sulfur, Worland, Wyo., made from hydrogen sulfide, at rate of 115,000 tons a year.

Figure 4. - Part of the crowd of 400 who made the tour of water-flooding projects arranged by Bureau of Mines engineers.

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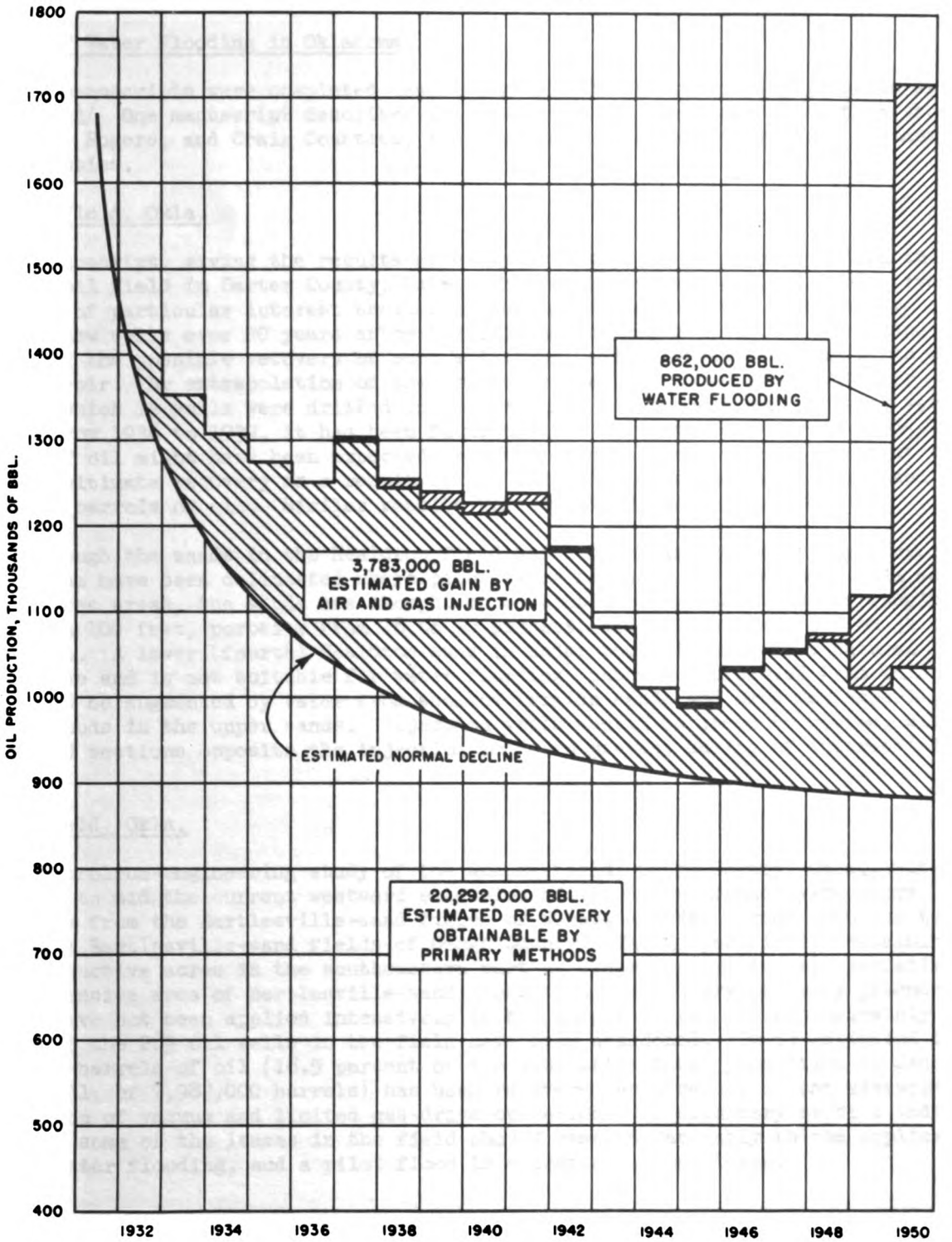

Figure 5. - Twenty-year oil-production history of Washington County, Okla., showing effect of secondary-recovery methods.

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History of Water Flooding in Oklahoma

Two manuscripts were completed describing all 180 water-flooding projects in Oklahoma.[14] One manuscript describes all operations in the State other than those in Nowata, Rogers, and Craig Counties, and the other described operations in these three counties.

Healdton Field, Okla.

A manuscript, giving the results of a 2-year study, is being prepared on the Healdton oil field in Carter County, Okla. This field, covering 7,500 productive acres, is of particular interest because of the increased recovery obtained by drilling new wells over 20 years after the original development of the field and because of the possible recovery of much additional oil by water flooding parts of the reservoir. By extrapolation of the production-decline curve of one 60-acre lease on which 13 wells were drilled in the original development and 11 wells were drilled from 1936 to 1939, it has been found that an ultimate recovery of 7,484,000 barrels of oil might have been expected from the original development, but that the probable ultimate recovery as a result of the infill drilling has been increased to 7,822,000 barrels of oil. Similar results were obtained on other leases.

Although the sands in the Healdton field are lenticular and interfingering, three areas have been delineated where pilot water floods are recommended. In each of the three areas, the sands are thought to be continuous, with thickness ranging from 20 to 100 feet, porosity from 18 to 30 percent, and oil saturation from 34 to 60 percent. A lower (fourth) Healdton sand is under the influence of a natural water drive and is not suitable for water flooding, but water produced from this sand could be augmented by water from shallow Permian sands and used for experimental floods in the upper sands. Injection wells should be cased to bottom, with perforated sections opposite the injection zones to prevent caving of interbedded shales.

Quapaw Field, Okla.

A petroleum-engineering study of the Quapaw field, Osage County, Okla., was initiated to aid the current westward extension of intensive secondary-recovery operations from the Bartlesville-sand fields of Nowata and Washington Counties to the deeper Bartlesville-sand fields of Osage County. The Quapaw field, containing 3,095 productive acres in the southeastern part of Osage County, is representative of an extensive area of Bartlesville-sand production. Secondary-recovery production methods have not been applied intensively in the Quapaw field, and approximately 65 percent of the 289 oil wells in the field have been abandoned. It is estimated that 1,470,000 barrels of oil (18.5 percent of the cumulative total production to January 1, 1951, of 7,987,000 barrels) has been recovered as a result of the widespread application of vacuum and limited gas-drive operations. Preliminary studies indicate that some of the leases in the field should respond favorably to the application of water flooding, and a pilot flood is operating on one lease.

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[14] Powell, John P., and Johnston, Kenneth H., A Survey of Oil Production in Oklahoma by Water Flooding. Part I. Nowata, Rogers, and Craig Counties, Okla.: Bureau of Mines Rept. of Investigations 4831, 1951, 160 pp.; Part II. Counties Other than Nowata, Rogers, and Craig: Bureau of Mines Rept. of Investigations 4832, 1951, 142 pp.

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Weber Pool, Okla.

Conditions in the Weber oil pool in Washington County, Okla., near Bartlesville and Dewey, are such that water flooding should increase the ultimate recovery substantially, according to a report[15] by Bureau of Mines engineers following a petroleum-engineering study of the field. Oil has been produced from the Bartlesville sand in the Weber pool at about 1,240 feet since 1905, when the discovery well was completed by T. N. Barnsdall. There were no restrictions on the rate of production from the field, and the reservoir energy was rapidly dissipated, causing the yearly production to drop from a peak of 2,500,000 barrels of oil in 1907 to 350,000 barrels only 4 years later. The application of vacuum to the producing wells, begun in 1914, slowed the decline. Gas injection into the producing formation, begun by one operator in 1926 and applied extensively by others beginning in 1937, appreciably stimulated the rate of production from many leases. It is estimated that from the date of discovery to the end of 1949 the field would have produced 10,400,000 barrels of oil without secondary-recovery operations, and that an additional 3,700,000 barrels was gained by using vacuum, drilling new wells, and injecting gas into the producing formation.

The oil saturation of the Weber-field reservoir still is high, and the physical characteristics of the reservoir make it well-suited for production by water flooding. The approximate 14 million barrels of oil produced through 1949 is equivalent to 5,300 barrels an acre, and it appears likely that water flooding in the field will make possible a further yield of about 5,000 barrels an acre. Four small water-flooding projects had been begun in the field when the report was completed, but they had not been in operation long enough to indicate the degree of success they will attain.

K.M.A. Field, Tex.

A petroleum-engineering study of the southwestern part of the K.M.A. field, Wichita and Archer Counties, Tex., has been completed.[16] The K.M.A. field is a large oil field controlled by many independent operators who voluntarily initiated a pressure-maintenance program soon after the field was developed. The Production Committee of the North Texas Oil and Gas Association requested the Bureau of Mines to prepare a report on this field, with the objectives of evaluating the pressure-maintenance program and investigating the possibilities of water flooding.

In addition to the development history and production records concerning the field, sample material-balance calculations and theoretical water-flood calculations are presented in the report. The discovery well that opened the southwestern part of the field for development was completed in 1937, and drilling continued until approximately 12,500 acres were delineated as oil-productive by the drilling of over 700 wells. Calculations in the report indicate that the gas pressure-maintenance program resulted in a 12.2-percent increase in oil recovery over recovery by primary production up to the closing date of the production statistics. Of the 168.1 million barrels of stock-tank oil originally in place in the reservoir, 27.4 percent had been recovered to August 1, 1949.

15/ Johnston, Kenneth H., and Moot, C. W., Jr., Petroleum Engineering Study of the Weber Pool, Washington County, Okla.: Bureau of Mines Rept. of Investigations 4740, 1950, 47 pp.

16/ Dobyns, Rollie P., Ayers, Marion L., and Lewis, Roger E., Petroleum-Engineering Study of K.M.A. Reservoir, Southwestern Part K.M.A. Oil Field, Wichita and Archer Counties, Tex.: Bureau of Mines Rept. of Investigations 4892, 1952, 88 pp.

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The theoretical performance of one 20-acre tract with a five-spot water-flood pattern indicates that approximately as much oil could be recovered from the tract by water flooding as had been recovered to August 1, 1949.

The gas pressure-maintenance program as outlined in the report should serve as a yardstick for the operators in their development of similar reservoirs, and the water-flood calculations predict the susceptibility of the reservoir to additional secondary-recovery methods by injecting water.

Cabin Creek Field, W. Va.

Engineers of the Franklin office completed an engineering study of the Cabin Creek field, Kanawha and Boone Counties, W. Va. The report[17] gives an engineering analysis of a 1,669-acre segment of the field, its development and operation from date of discovery in 1917 to date of probable abandonment, estimates of total oil to be recovered, and the quantity of oil remaining in the sand. Surface maps of the property and isopachous and contour maps of the sand are presented.

The engineering study shows that the cumulative oil produced from the Cabin Creek field, in 18 years of primary-recovery operation, amounted to 15 percent of the original oil in place. In addition, during the years of primary recovery and 10 years of secondary-recovery gas-drive operations, 21.2 percent of the original oil was produced; and, using the same production techniques and 25 more years of operation, before probable abandonment the total oil recovered would amount to 25.6 percent of that originally in the reservoir. Furthermore, the oil saturation at estimated abandonment date would be 54.9 percent of total pore volume. The engineering study indicates the probability of recovering considerable additional oil by water flooding, which was begun experimentally in this part of the field in 1948.

Engineering field studies of several air-gas injection projects in the Oil City-Titusville (Pa.) area reached various stages of completion; these studies supplement those being made on the application of siphon flowing of oil from wells on air-gas injection projects.

Survey of Secondary-Recovery Operations in California

A secondary-recovery program of field and laboratory studies in California, begun in 1950, is designed to provide better knowledge and understanding of the problems involved in achieving increased oil recovery by secondary methods, particularly water flooding, in this State. These problems, not common to such operations in the eastern and midcontinent fields, stem from greater sand thicknesses and variations in sand permeability, as well as higher oil viscosity and greater reservoir depth. To furnish a background of information on current secondary-recovery operations in California, a survey has been made of representative gas- and water-injection projects. The manuscript of a report on the study, which includes 12 gas-injection and 4 water-injection projects, has been published.[18] The report describes the

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17/ Magee, Joe N., and Taylor, Sam S., Petroleum-Engineering Study of Gas-Injection Operations in the Cabin Creek Field, Kanawha and Boone Counties, W. Va.: Bureau of Mines Rept. of Investigations. In press.

18/ Loomis, A. G., Fried, A. N., and Crowell, D. C., Recovery of Oil in California by Secondary Methods. Part I. San Joaquin Valley Oil Fields: Bureau of Mines Rept. of Investigations 4886. In press; Part II. Los Angeles Basin and Coastal Oil Fields: Bureau of Mines Rept. of Investigations 4887, 1951, 46 pp.

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development and operation of the individual fields and the characteristics of the reservoirs and reservoir fluids. It also includes their production histories and analyzes the effects of gas injection and water injection on sustaining or improving the productive capacities of the fields. In fields where the results were unfavorable, an analysis is given of the conditions that adversely affected the efficiency of the injected fluid in displacing oil from the reservoir rock or in augmenting the available expulsive reservoir energy.

Certain general conclusions may be drawn from the information in the report. By and large, the results of current secondary-recovery projects in California indicate that gas and water injection can increase the recoverable oil reserves of California materially when such methods are utilized with appropriate controls. In some instances, where initial attempts to augment natural reservoir energy by gas or water injection were unsuccessful, the primary deterrent was lack of control over the migration and distribution of the injected medium. By means of the newly developed techniques in well logging and use of tracers and by making temperature, pressure, gas-oil-ratio, and water-oil-ratio surveys, operators were able to determine the points of entry of the injected medium into the sands and follow its areal distribution. Thus, they were able to take appropriate steps to bring about the most efficient utilization of the injected medium.

In fields where gas or water is injected into a number of oil sands exposed in the injection well, the large difference in permeability between individual sands results in dissemination of most of the injected fluid through strata having high permeability, which have been largely depleted of oil during the primary-production history of the field. In many such instances, application of selective injection into individual sand bodies has been a successful solution to the problem. In some fields, where miltiple sands with high vertical variation in permeability do not present the chief obstacle to efficient injection, the condition of high lateral variation in permeability has caused channeling of the injected medium through areas of such limited extent that neither reservoir pressure nor oil production was benefited. This condition has been alleviated to some degree by close control over production allocation between wells, by shutting in wells in which the produced gas-oil or water-oil ratios become excessive and by adjusting injected volumes, or altering injection-well patterns. In many of the fields studied, benefits derived from the secondary-recovery project could not be measured in terms of production of oil over and above the quantity that would have been produced by primary methods alone. Benefits of the injection process in these fields were noted: (1) By an increase in reservoir pressure or a reduced rate of decline of reservoir pressure; (2) by improvement in produced water-oil or gas-oil ratios; (3) by formation of gas caps or extension of existing gas caps; (4) by extension of the flowing life of wells; (5) by control of edge-water encroachment; and (6) by improved productivity indexes of wells. In addition to its value in presenting factual and interpretive data, the report serves to point up the necessity for further field and laboratory study of secondary-recovery problems.

Special Field Problems

Location of Abandoned Wells

Improperly abandoned wells, on which there are no records, are a source of trouble on most water-flooding projects in the old, shallow fields of Kansas and Oklahoma. These wells result in the loss of water and oil to the surface or to shallower porous zones and usually are difficult and expensive to find. Bureau engineers have found some simple devices that are frequently helpful with this

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problem, but its complete solution has not been reached. Pipe finders, such as are used by water and gas-service companies, may provide a clue to the location of old wells, as they show the position of old lead lines if they have not been removed. Much scrap iron is left around old well sites, and this material can be found with a mine detector, indicating the general location of the wells. If pipe has been left in the well, it can be located accurately by a dip needle, as the pipe is always highly magnetized. In spite of considerable research, no method has been found to locate accurately wells from which all the pipe has been removed. A report giving the results of this work is being prepared.

Conditioning Water for Subsurface Injection

A field study of plants conditioning water for subsurface injection was completed, and a final report on the study is being prepared. Intensive studies were made of 25 plants in Kansas, Oklahoma, and north Texas. The studies included determination of corrosivity, stability, chemical composition, and organic content of water samples and collection and tabulation of engineering data pertaining to the type of equipment used.

The water-conditioning systems studied were evaluated as to comparative efficiency in minimizing the corrosiveness of different kinds of water and in stabilizing the waters to prevent plugging of pores of the oil-producing formation by precipitated solids. A summary of data for all systems studied is to be presented in the report; and nine of the systems, which are representative of different conditioning methods, are to be described in detail, with the aid of flow diagrams, property maps, and photographs of the equipment. The report should be an excellent guide for the design and operation of a water-treating plant, as the study was more thorough than any made previously.

The supply of reprints of an earlier journal article,19/ describing tests and analytical procedures used in the study of water-treating plants, has been exhausted, and the article is being revised for publication as a report of investigations. A paper describing the work presented at the 117th Annual Meeting of the American Chemical Society in Houston, Tex., in March 1950 was published in a trade journal.20/ The work has shown that: (1) Many operators do not make adequate checks on the plant operation; (2) better design of sedimentation ponds and tanks is needed to assure more complete coagulation and precipitation; (3) corrosion is, in general, a more serious problem than plugging of the oil sand in the Midcontinent area; (4) closed systems may be used successfully for handling waters having negligible acidic gas concentrations and low iron and suspended solids contents; and (5) additional study is needed of the deaeration and degasification of waters and the correlation of alkalinity and carbonate stability with the quantity of lime and other alkalies added.

Selective Plugging

Although shop and field tests disclosed many modifications and improvements needed in the small-diameter well caliper, which has been developed during the past

19/ Watkins, J. Wade, Corrosion and Chemical Testing of Waters for Subsurface Injection: Producers Monthly, vol. 14, No. 4, February 1950, pp. 15-19; No. 5, March 1950, pp. 30-31, and No. 6, April 1950, pp. 25-31.

20/ Watkins, J. Wade, Arthur, C. E., and Willett, F. R., Jr., Field Laboratory Studies of Methods of Conditioning Waters for Subsurface Injection: Oil and Gas Jour., vol. 49, No. 15, Aug. 17, 1950, pp. 120, 122, 124, 127-128.

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2 years, the instrument is complete now and has been put into field use. This makes available for the first time a caliper that can be run through 2-inch tubing used in completing many water-injection wells. The instrument is 1-3/4 inches in diameter and slightly less than 6 feet in length. It is run on a single-conductor electric cable and has four caliper arms capable of measuring holes 6 to 36 inches in diameter with an accuracy of ± 1/4 inch and has other facilities to indicate at the surface the position of each arm separately.

Selective Plugging of Air-Gas Injection Wells

Oil recovery by gas injection is hindered seriously on some secondary-recovery projects because of bypassing of much of the injected gas. Bypassing develops in reservoirs that are composed of strata of widely varying permeability. In each stratum the effective permeability to gas increases rapidly as the liquid (oil and water) saturation is decreased. When a reservoir is subjected to gas injection, the strata possessing the highest permeability to gas are depleted of oil before the remainder of the sand. Unless movement of gas through these strata can be restricted, they continue to transmit gas from injection wells to producing wells during the whole life of the project. Selective plugging of these essentially depleted sections of oil sand, to prohibit or minimize bypassing of the injected gas that does no useful work, is one of the most-important problems confronting operators of gas-injection projects. Simply, the reason is that to compress gas is costly, and less oil will have been recovered at the time the project ceases to make a profit. In the Appalachian region the most urgent need for work on selective plugging is development of techniques in applying suspensions of solids in gas or liquids in gas-injection wells.

Pennsylvania State College and other organizations have completed substantial laboratory work on plugging small sandstone specimens with various smokes and liquids, but none of these products has been applied successfully on a gas-injection project. One product has been applied successfully, however, by operators of water-flooding projects in the Bradford, Pa., field. Laboratory experiments showed that this plugging agent, a water emulsion of resin having a particle size of 0.6 micron, might be applied successfully to plug sands having much larger pore diameters than occur in the Bradford sand because the size of the resin particles can be adjusted reliably between the limits of 0.6 and 93.0 microns by adding small amounts of sodium carboxymethylcellulose. The laboratory work showed further that the emulsion might be applied to a gas-injection well using substantially the same procedures applied to achieve selective plugging of water-injection wells in the Bradford field, provided enough water was injected into the gas-injection well just before plugging.

An interested operator provided a test area on a 13-year-old gas-injection project in the Goodwill Hill-Grand Valley field. Bureau engineers equipped each of the 6 injection wells and 15 oil wells in the area with recording flowmeters to measure the rates of gas production and injection. The operator equipped each oil well with a tank to gage rates of oil and water production. These data were recorded for long periods before and after water and resin were introduced into the injection wells. Many injectivity tests were made on the injection wells before and after plugging.

The published results of the field test[21/] show a marked decrease in injection capacity resulted from the treatments, but only negligible changes occurred in the

21/ Bail, Paul T., and Whieldon, Charles E., Jr., Selective Plugging Experiments on Gas-Injection Wells in Western Pennsylvania: Producers Monthly, vol. 15, No. 3, January 1951, pp. 25-35.

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oil-, water-, and gas-production rates of the 15 oil wells. It was concluded that the plugging was not selective (that is, did not change the distribution of injected gas between beds of sand within the wells). According to recent injection tests, the plugging effects obtained in the injection wells by the treatment were still present 12 and 18 months after the separate plugging treatments.

At the conclusion of this experiment, attention was directed to a means of generating a smoke (solid particles suspended in a gas phase) within an operating injection well opposite the sand face. Titanium tetrachloride, which reacts with water vapor to produce titanium dioxide smoke, appears promising in preliminary laboratory tests. An apparatus to test thoroughly the plugging effect of this smoke, generated under pressure, is being built.

Flowing of Oil Wells on Gas-Injection Projects

On a gas-injection project, when the oil-production rate reaches a low level and operational costs continue to increase, the operator faces the alternatives of abandoning the property or initiating more efficient production techniques. Mainly responsible for the high operational costs is frequent pulling of well equipment for repair of sucker-rod pumps. Additionally, as the project gets older, excessive by-passing of the injected gas - or air-gas mixture - occurs, pyramiding compression costs on the pump-repair costs as the oil income declines. Although coming at a time when the operator can least afford it, an additional capital investment usually is necessary to accomplish a more profitable operation of a project in this category. It has been established, however, by study of many similar projects, that enough oil usually remains in the reservoir to warrant the new exploitation, and profitable operations result if the more efficient techniques are applied diligently.

To avoid the excessive oil-lifting costs of frequent pump repair, intermittent pumping of small oil wells in the Oil City, Pa., area has been replaced on some leases with intermittent flowing of the production. Bureau engineers reasoned that the injected gas that moved the oil through the reservoir to the oil wells retained enough residual energy to lift the oil and water production to the surface through properly designed siphon flow-strings.

Laboratory and field experiments have proved that small quantities of oil and water could be flowed to the surface satisfactorily through 1-inch-diameter siphon flow strings containing a certain number and size of gas-inlet orifices drilled in the pipe at a certain place - usually adjacent to the top of the sand. Most wells tested, ranging in depth from 300 to 1,100 feet, have been made to flow automatically without any expensive valving arrangement, but a few wells where reservoir pressures have not been elevated enough have required stopcocking, either automatically with instruments or manually.

On July 1, 1951, about 200 flowing wells on gas-injection projects in the Oil City-Pleasantville-Titusville (Pa.) area were equipped with flow strings designed by Bureau engineers, on 19 leases operated by 5 companies. About 150 of these flowing wells are on a group of adjacent leases, and 81 of them are operated on one lease.

Work during 1951 included the continuous accumulation of data, utilizing Bureau instrumentation, on projects under study. A comprehensive engineering appraisal of a new group of leases near Titusville is being conducted to determine if flowing the oil wells would help keep the property in profitable operation. The company faced the choice of abandoning the leases when they ceased to produce oil at a profit by the production practice in vogue or of purchasing another compressor to increase

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injection volumes that would be necessary to flow all the wells. Preliminary studies indicate that the wells on the poorest lease could be made to flow and produce oil at a profit.

During the year the practice of flowing oil wells on gas-injection projects, developed by the Bureau's engineers in Pennsylvania, was introduced into the Mid-continent area. Five stripper wells in the West Colony, Kans., field have been converted from pumping to flowing with 1-inch siphon flow strings. The method of flowing these wells differs from that used in Pennsylvania, as these wells do not contain casing but are completed with 2-inch tubing cemented at the top of the oil sand. Wells completed with tubing have much less storage space for gas than those completed with casing but are being flowed successfully by use of improved automatic flow controllers.

Relationship of Water-Injection Rate to Reservoir Saturation

Water-injection tests were continued on a 60-acre water-flooding project in the Bartlesville-Dewey field, Washington County, Okla., to establish the relationship between intake capacities of the input wells and saturation of the sandstone formation. The total quantity of water injected to the time production was stimulated in the first three newly drilled oil wells on the project exceeded the quantity that was calculated to saturate completely the 60-acre reservoir because of loss of water to the edges. However, the over-all effect of the injected water cannot be ascertained fully until the rest of the producing wells are drilled.

Effects of Cold-Water Injection on Oil Recovery

In the Bradford field, ultimate oil recovery probably will not exceed 60 percent of the oil originally in place, even on leases subjected to the best-known water-flooding technology. Conservation-minded operators and researchers have long pondered the possible effects on oil recovery of the 30 or more years of sustained injection of cold water into the Third Bradford sand. As some leases are being water-flooded for the third or fourth time, utilizing the constantly improved technologic practices and considering the highly paraffinic nature of the crude oil, operators have wondered if the reservoir had been cooled enough to cause precipitation of waxes in the reservoir.

To provide information on this thought-provoking problem, engineers at the Bureau's Bradford office measured subsurface temperatures and conducted laboratory tests on subsurface and wellhead oil samples. Temperature measurements in 42 widely separated wells indicate that reservoir temperatures range from 59.7° F. at 1,150 feet to 71.9° F. at 2,040 feet. Temperatures in newly drilled wells were higher, by as much as 4.5° F., than in old oil wells. Temperatures of the water entering the sand in some wells were 11.5° F. lower than reservoir temperatures before injection.

Wax-precipitation temperatures measured on 26 samples of oil, including 7 subsurface samples, ranged from 51° to 67° F. It was significantly noted that the wax-precipitation temperatures of oil samples from the leases subjected to water flooding were consistently higher than on leases where flooding had not been initiated. On water-flood leases, the wax-precipitation temperatures ranged from 58° to 67° F., with wax contents from 2.57 to 3.42 weight percent, whereas, on property that had not been water-flooded, the wax-precipitation temperatures ranged from 51° to 58° F., with wax contents from 2.20 to 2.97 weight percent. Wax-precipitation temperatures on one sample were increased 3.5° F. by liberating dissolved gas by pressure reduction from 204.4 p.s.i.a. to atmospheric pressure and 10.0° F. from atmospheric pressure to 0.2 p.s.i.a.

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A report[22] describing this work gives experimental evidence and concludes that deposition of solid wax in the reservoir might occur, as cold-water injection not only causes a reduction of reservoir temperatures but alters the composition of reservoir oil by absorbing light hydrocarbon constituents from the oil. This absorption of hydrocarbons in water under high pressure might continue until the wax-precipitation temperature of the oil is elevated to the temperature of the reservoir, at which time wax will precipitate from the oil.

Shooting Oil and Gas Wells with Explosives

The physical and chemical behavior of explosives is well-known, but the effects of explosives in breaking rocks in oil and gas wells are not known with any degree of exactness. Unfortunately, the oil and gas industries can measure the effects of a shot only indirectly through increase in the conductivity or productivity of the well and, to a questionable extent, in terms of the amount of crushed rock cleaned from the well after the shot. Direct measurement or examination of the fractures caused by the shot that results in the increased conductivity of the well is not possible. Thus, the mechanism of fracturing a reservoir rock in a well bore with an explosive can be only postulated. To improve the empirical methods now used in designing shots for oil and gas wells, it will be necessary to explore the fundamental relationships governing the fracturing of rocks under controlled conditions. Fortunately, the Applied Physics Branch of the Bureau has been working during the past few years on mining problems to determine the behavior of rocks when subjected to dynamic or shock loading and has developed techniques of measuring the strain produced in rocks by shock wave resulting from an explosive detonated within a rock. The instrumentation techniques and knowledge of rock characteristics thus developed have permitted an experimental approach to the problems of oil-well shooting that promises a direct correlation between the effects of different explosives (or between the methods of loading, tamping, and detonating any one explosive) and at least some of the physical properties of rocks, as determined by laboratory measurements on core samples.

An experimental program of shooting boreholes drilled to shallow depths in a sandstone thick enough and exhibiting lithological properties comparable to reservoir rocks has been initiated. The shots are instrumented by using electrical resistance-type strain gages or piezo-electric crystal-type pressure gages in nearby boreholes to determine the strain or pressure produced in the rock by detonated explosives. The gages provide a means of judging the extent of fracturing to be expected, and water-injectivity tests on a shot-hole before and after the shooting show the increased conductivity. Preliminary tests were conducted on a lease 3.5 miles from Franklin, Pa., where a 50-foot section of Homewood sandstone (Pottsville group of lower Pennsylvanian age) occurs under a thin cover of soil and clay. A report[23] describing four series of field experiments conducted during the summer of 1949 gives evidence that the type of instrumentation chosen met the experimental conditions adequately and provided quantitative data from which the generation and propagation characteristics of the explosive wave could be calculated.

22/ Sayre, Allyn T., and Wertman, W. T., Effects of Water Flooding on Reservoir Temperatures and Wax Precipitation in the Bradford, Pa., Oil Field: Bureau of Mines Rept. of Investigations, 4842, 1952, 34 pp.

23/ Grant, Bruce F., Duvall, Wilbur I., Obert, Leonard, Rough, R. L., and Atchison, T. C., Use of Explosives in Oil and Gas Wells - 1949 Test Results: Bureau of Mines Rept. of Investigations 4714, 1950, 29 pp.

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Following completion of the 1949 tests, a comprehensive program of field and laboratory experiments was planned. During the spring and summer of 1950 part of the planned field experiments were conducted. Fifteen holes 130 to 160 feet deep and 148 holes 20 to 30 feet deep, aggregating a total footage of 6,206 feet, were diamond-core-drilled into the same Homewood sandstone as in the preliminary experiments. Some experimental-type diamond bits were utilized, and drilling-performance data were provided the Bureau's Mount Weather (Va.) Station, where drilling research for mining is conducted. The rock core was used at laboratories at Franklin and at College Park, Md., in determining the physical properties of the sandstone for correlation with the strain wave and pressure data taken during the shooting tests. The boreholes ranged in diameter from 2.33 (BX size) to 8 inches, but most of the footage drilled was 2.95 (NX size) inches.

All of the experiments planned for the summer were not completed, but 26 experimental shots were detonated. One series of shots compared radial compressive strains detected with S-4 gages cemented under water and pressures detected with tourmaline gages suspended in water-filled holes. An empirical relation was found between compressive strain data and pressure, but additional tests must be made to provide a qualitative relation between dilatation as measured with strain gages and pressure in order that the cheaper, more easily placed pressure gages may be used in instrumenting shots in wet rock. A second series of shots compared strain produced by explosive charges of the same size with varied amounts and kinds of stemming. Each type of stemming exhibited an optimum height above and below which the rock was subjected to less than maximum strain. Optimum stemming was found to be the height of column (water or wet sand) that just confined the detonated charge. Optimum stemming resulted in strains in the rock at least 50 percent greater than when identical charges were detonated, either without stemming or with maximum stemming. A third series compared strain while varying the diameter (length a constant) of cylindrical charges (1.75- to 7-inch). A fourth series of tests compared strains produced while varying the length (diameter a constant) of cylindrical charges. These tests indicate that strain at a distance less than three times the length of the charge is not increased by further increase in charge length. A fifth series compared strains produced by different explosives (charge weight constant): 60 percent seismograph gelatin, 40 and 90 percent high-velocity gelatins, and liquid nitroglycerin. Only a few shots of this series were completed, but it is evident that the test procedure can define relatively small differences in the characteristics of explosion waves from different explosives.

Laboratory experiments on the physical properties of reservoir rocks were completed on 126 rotary-core samples procured from operators of oil and gas fields in the Appalachian, Midcontinent, and Rocky Mountain regions. The physical-property tests were conducted by the Bureau's Applied Physics Branch at College Park, Md., and included: (1) Apparent specific gravity; (2) apparent porosity; (3) compressive strength; (4) modulus of rupture; (5) impact toughness; (6) Young's modulus; (7) modulus of rigidity; (8) specific dampening capacity; (9) apparent Poisson's ratio; (10) velocity of sound; (11) scleroscope hardness; and (12) abrasive hardness. In addition, an impact test to determine the breaking strain under high-speed dynamic loading of disks of core was developed, which, it is conceived, may provide criteria for shot design. Correlation of these physical property data indicates the significant conclusion that future testing can be confined to the measurement of only two rock properties - scleroscope hardness and apparent specific gravity - with other properties closely estimated from these two easily made tests.

To supplement the physical property testing of reservoir rocks at College Park, equipment was fabricated at the Franklin laboratory to measure the porosity of NX

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size specimens 4 inches long and the liquid permeability of NX size specimens ranging in length from 0.25 to 14.00 inches. The porosimeter is the Boyle's Law gas-expansion type, whereas the permeameter is designed to use any fluid likely to be encountered in an oil reservoir but will be operated at low pressure. When water is to be used as the fluid in measuring permeability, a standard buffered brine containing no dissolved oxygen will be employed. Utilizing this apparatus, rock specimens of any size needed by the College Park staff for proposed tests in determining the effects of varying gas, oil, and water saturations on standardized physical property tests can be provided. These units of equipment are nearing completion. Obviously the data acquired with them will be used in all studies in progress involving reservoir engineering.

Laboratory Studies

Core and Water Laboratories

The volume of work performed by the core- and water-analysis laboratory at the Bartlesville Station increased appreciably because of the demand for core analyses as a part of the petroleum-engineering study in Scurry and adjacent counties in Texas (described earlier in this report) and a survey of oil-field brines produced in Kansas. The demand for analyses of oil-field brines has increased sharply during recent months because this basic information is needed for the quantitative analysis of electric logs by newly developed methods. To provide this information on brines from Kansas oil fields, over 500 samples of brines from fields all over the State have been collected for analysis. Complete mineral analyses and resistivity measurements at four temperatures have been completed on over 400 of these samples. As soon as this work can be completed, a report giving the results of the analyses will be prepared for publication.

The core-analysis work included 685 permeability measurements, 661 porosity measurements, 340 determinations of connate water by the evaporation method, and 18 determinations by the restored-state method. Most of the cores tested were from carbonate reservoirs. These cores vary so much in their physical characteristics that the 3/4-inch-diameter by 1-inch-long samples previously used for porosity and permeability are too small to be representative. To provide more-reliable measurements, the porosity and permeability equipment was modified to use samples 1-1/2 inches in diameter by 2 inches in length. Samples of this size can be tested almost as rapidly as the smaller samples; but, being approximately eight times as large, they provide a far more representative sample. The Bureau's core laboratory at Dallas, Tex., collaborated in preparing and analyzing limestone cores from the reef fields of Texas.

Oil-formation specimens procured in the Appalachian region from wells drilled on secondary-recovery projects, and others obtained in connection with special scientific investigations of reservoir characteristics being studied by Bureau engineers, are analyzed in the Franklin laboratory. Cores are tested, after preparation with special tools, for porosity, permeability, oil and water saturation, and the chloride content of the contained water. During the year, two gas-well cores from gas-storage reservoirs were analyzed in connection with the studies on shooting oil and gas wells with explosives described elsewhere in this report.

Much oil is found in reservoirs in formations of the Cretaceous period, and most of the old fields in the Rocky Mountain region produced from these formations. Whenever possible, cores from wells being drilled in these formations are being acquired and are being studied in the laboratory at the Laramie Station. Characteristics of the rocks, flow of fluids through them, recovery of oil by flooding or

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driving agents, and other data having a bearing on the recovery of more oil from these old fields are being obtained.

Recovery Efficiency of Water-Flooding High-Viscosity Oils

During the year laboratory apparatus was designed and built in the San Francisco laboratory to determine the efficiency with which oil sands containing residual quantities of high-viscosity oils can be water-flooded, and the experiments have been begun. (See fig. 6.) In this equipment previously prepared cores mounted in plastic and containing known quantities of oil and brine are flooded with a brine at a constant rate. The final saturation is determined by material balance using calibrated cylinders to measure the recovered volumes of oil and water. Each test is conducted with successively more viscous oil, within the range of viscosity found in California fields.

The versatility inherent in the design of the apparatus permits wide latitude in the types of experiments that can be conducted. For example, with only minor changes in the apparatus, the influence on oil recovery of different pressures, flooding rates, and sand permeability are to be determined. Moreover, the efficacy of carbonated water and various surface-tension-reducing agents and the effect of the presence of free gas in the reservoir are to be tested.

Correlation of Residual Oil Saturation, after Laboratory Air-Drive Tests, with Pore Pattern of Sandstones

Air-drive experiments, utilizing reservoir sandstone specimens saturated partly with native crude oils and brines, had been conducted in the Franklin laboratory to determine if a mathematical formula could be established to equate oil recovery with other data that could be derived readily in the laboratory by analyzing rock cores and crude oils. An equation was formulated; but, in order to fit all the experimental data into the one relationship, constants of significant order had to be employed. It was observed that, although each experiment was terminated at exactly the same produced air-oil ratio (comparable to economic field practice), the quantity of oil retained in each rock specimen differed greatly. Although sand grain-size and grain-distribution data had been included in the derived relationship, it was recognized that surface-energy phenomena, influenced by the size, shape, and distribution of rock pores and their connecting capillaries, were mainly responsible for the differing amounts of residual oil. Obviously a comprehensive pore-pattern study was needed to shed more light on the technical factors grouped into the constants of the mathematical formula. To observe representative pores and make pictorial records for study, it was apparent that the investigation would have to be approached by utilization of microscopy and thin sections, even though examination of such small pieces of rock only 0.001 inch thick would require a tedious, time-consuming, but comprehensive statistical analysis of data on scores of thin sections.

Eight thin sections, perpendicular to the direction of flow, were prepared from each radial sandstone specimen used in the laboratory air-drive experiments. Color photomicrographs were made of each thin section of plastic-impregnated sandstone, and pore cross-sectional areas were computed from measurements made on projections of the color photomicrographs. During the year thousands of pore cross-sectional areas have been determined, and statistical analysis is well under way. Plotting residual liquid saturations against "n" values (a pore size-distribution factor determined for each rock specimen) the maximum deviation of datum points is within 4.5 percent of the mean established trend. Specific surface areas are being determined for use in the final mathematical relationship between pore size and shape and the residual oil left in the sandstone specimens following the air-drive experiments.

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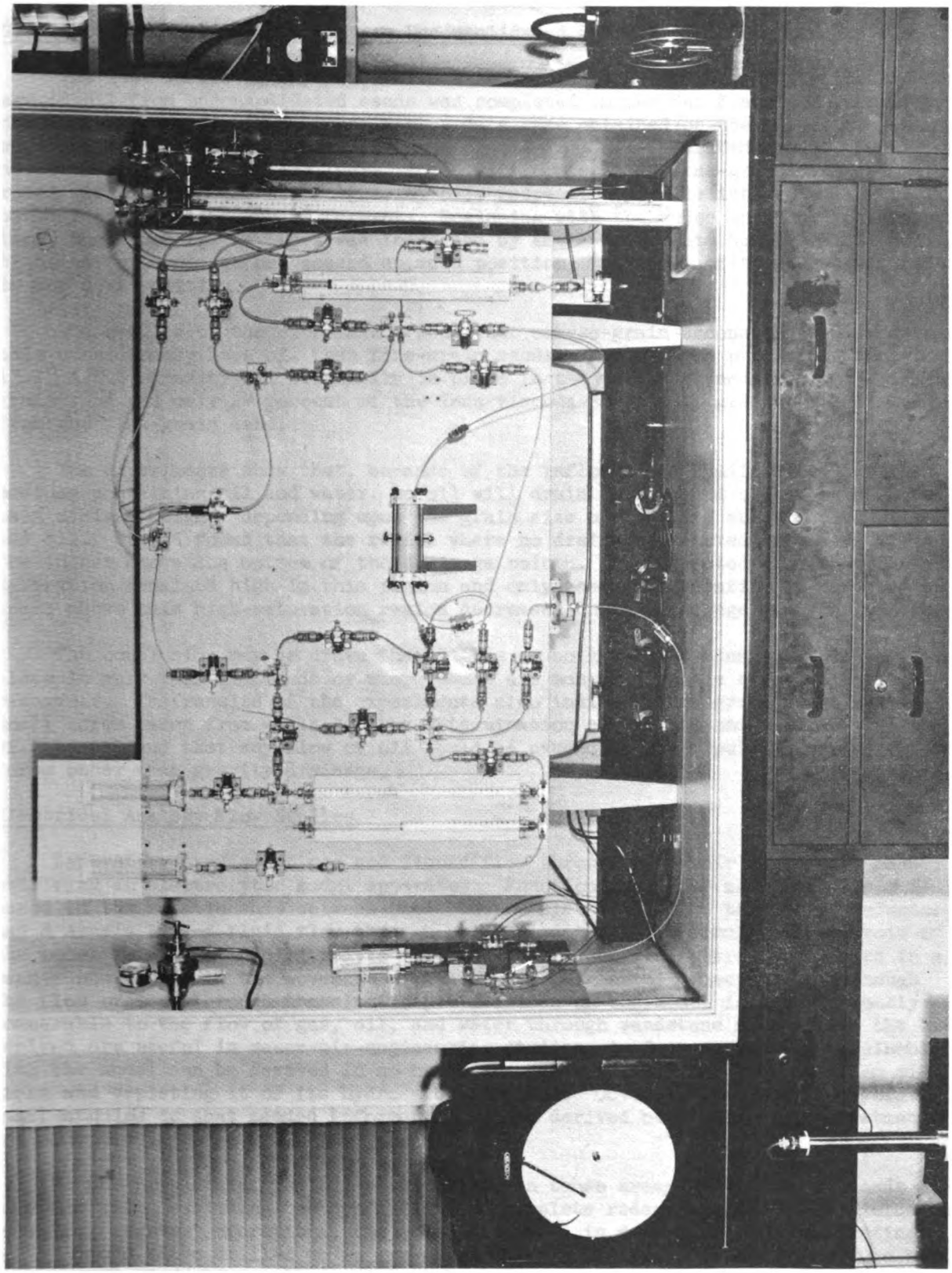

Figure 6. • Apparatus assembly for determining recovery efficiency of water flooding high-viscosity oils.

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Gravitational Drainage of Oil from Unconsolidated Sands

The last series of experiments in a long-term study of the gravitational drainage of oil from unconsolidated sands was completed in the San Francisco laboratory during the year. In these experiments, data were obtained on the effect of grain size and A.P.I. gravity on the drainage of oil from oil-saturated sands. Two 2-inch steel tubes, 24 inches long, were packed with coarse- and fine-grain sand and saturated with 13° and 38° A.P.I. gravity oil, respectively. The interstitial water content of each sand was 25 percent. Beginning with the tubes in a horizontal position, the slope of the tubes was increased by small increments to a vertical position. After drainage had ceased at each position, the slope of the tubes was raised to the next position.

The results of the experiments show that coarse-grain unconsolidated sands retain considerably less oil than fine-grain sands. Fifty-seven percent of the viscous 13.1° A.P.I. gravity oil originally in place in the pores drained from the coarse-grain sand and only 24 percent of the less viscous 38° A.P.I. gravity oil drained from the fine-grain sand.

The experiments show that, because of the influence of capillarity in porous mediums containing oil and water, no oil will drain from a sand column below a certain minimum height, depending upon the grain size of the sand and the viscosity of the oil. It was found that the region where no drainage occurred extended only a few inches above the bottom of the drainage column. It was noted also that the oil saturation remained high in this region and only the oil saturation in the pore space above this high-saturation region decreased during drainage from the column.

The conclusion may be drawn that little or no gravity drainage of oil takes place in very thin flat beds or where there are many flat shale streaks in a sand reservoir. The results of the experiments also indicate that gravity drainage from small cores taken from wells for the determination of the oil and water saturation will be nil and that any flow of oil would be caused by the expulsion by gas or some force other than gravity drainage.

Electrical Analogy Flow Studies

Laboratory studies of gas and liquid flow through reservoir rocks were made utilizing an electrolytic model apparatus. Functioning of the model oil field is based on the relationship between Ohm's law of electrical flow through a conductor and d'Arcy's law of fluid flow through porous mediums. The simulated reservoir of the model is a gelatin electrolyte through which electrical current is passed in a manner comparable to the movement of gas or water in an oil reservoir. Although the flow of ions through the electrolyte utilized in the model is not rigorously comparable to the flow of gas, oil, and water through sandstone reservoirs, the data derived are useful in reservoir-engineering studies; in fact, some data obtainable with the model can be derived in no other way, except partly by developing an oil field and depleting it of its hydrocarbon content. Obviously the advantage of the model studies is that needed information can be derived before capital investments are committed.

In the Appalachian region, particularly in those areas where the oil sands are deep and thin, excluding the probability of complete redevelopment of old fields for secondary-recovery operations, the model is useful in determining which existing wells, among those drilled to an irregular pattern and spacing, may be used to best advantage as injection wells to drive the greatest quantity of oil to the producing

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wells with the expenditure of the least amount of energy. Thus, a choice of wells most likely to lend themselves to the most efficient operation of the field can be made before the expenditure of redevelopment capital. Moreover, if it is economically feasible to redevelop a field completely, or partly, by drilling new wells, the model can be used to determine proper spacing and pattern of the wells to be drilled. The greater the knowledge of the physical characteristics of the reservoir rock and its fluid contents, the nearer one can estimate the optimum well pattern that will contribute to more efficient extraction of oil from a field.

The model is better suited to studies of water-flooding problems; but, by employing the gas laws, including perfect-gas-deviation factors and additional reservoir data, the model provides equally pertinent information on gas-injection problems.

The electrolytic model was used in a study of a segment of the Paola shoestring-sand oil pool in Kansas to compare the relative volumetric efficiencies of various water-flooding techniques and well patterns of proposed new wells to be drilled. The river-channel shape and the permeability characteristics of the reservoir imposed limitations to the positioning of wells that are peculiar to this type of oil pool. A report[24] describing the 10 electrolytic model tests showed that the volumetric flood efficiencies of the well patterns investigated would range from 60 to 96 percent. Development and water costs were computed to be 19 cents for each barrel of oil to be recovered by the most efficient method.

Electrolytic-model tests were made on a West Virginia oil field[25] on which Bureau engineers had previously conducted exhaustive engineering field studies (results published). The model tests indicated that the operator of the Boggs field could recover by gas-drive operations 95,000 additional barrels of oil without drilling any new wells or injecting any greater quantities of gas by using five injection wells properly located (considering the reservoir characteristics) instead of the three injection wells now used. Other tests made on the Boggs field indicate that, if the operator should elect to water-flood the field, 3,100,000 additional barrels of oil could be produced. Increasing the ultimate recovery that much, however, would require the operator to drill 17 new wells at selected locations.

Corrosion of Metals by Dissolved Gases in Water

Tests were continued in the laboratory at the Bartlesville Station to determine the corrosiveness of water containing dissolved gases (oxygen, free carbon dioxide, and hydrogen sulfide) on metals, when other controllable factors contributing to corrosion are maintained constant. Curves have been developed from the data obtained in numerous tests, in which corrosivity, as expressed in the weight loss of metal, is plotted against the concentration of dissolved gas in water acting as a corroding medium. One curve expresses the corrosivity of dissolved oxygen and a second that of dissolved free carbon dioxide, each in varying concentrations. A third curve expresses the corrosivity of varying concentrations of dissolved free carbon dioxide combined with a constant concentration of dissolved oxygen. Tests are being continued using water containing varying concentrations of dissolved oxygen and a fixed concentration of dissolved free carbon dioxide as the corroding agents. The results

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24/ Eckard, William E., and Mason, Jack A., Electrolytic Model Studies as Applied to Water-Flooding a Shoestring Sand: Bureau of Mines Rept. of Investigations 4778, 1951, 18 pp.

25/ Tignor, E. M., Jennings, T., and Krause, L., Secondary Recovery of Oil by Gas Injection in the Boggs Field, Roane Co., W. Va.: Bureau of Mines Rept. of Investigations 4430, 1949, 31 pp.

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Figure 7. - Radiation-detecting equipment used in radiochemical laboratory.

Figure 8. - Improved all-glass liquid-permeability apparatus in thermostatically controlled bath.

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of the study will provide corrosion data needed for the efficient operation of water-treating plants. Also, they will assist in the modification of existing and the development of new water-conditioning methods designed to minimize corrosion in plants that condition water for secondary recovery of oil, reservoir-pressure maintenance, and brine disposal.

Tracers in Waters Used for Subsurface Injection

The small radiochemical laboratory at the Bartlesville Station, reported last year as being under construction, has been constructed, equipped, and is being used to study radioactive isotopes as tracers. Figure 7 shows radiation-detection equipment being used in the instrument room of the new building. Studies of the performance of reservoirs under a natural water drive, pressure maintenance by water injection, or water flooding would be expedited greatly if a tracer were available that might be added to injection water at input wells and detected qualitatively, or preferably, quantitatively, in small concentrations at oil-producing wells. No such tracer is known, although a wide variety of materials have been tried, including sugar and a number of dyes. Very little information that will serve as a guide in the study is available in the technical literature. The greatest problem in the development of a suitable tracer is adsorption of the tracer on the reservoir rock. Work has been begun on sealing in plastic sandstone sections and cores, cut horizontally with the bedding planes of the formation, for use in a laboratory study of the adsorptive characteristics of various stable forms of elements and compounds that may be of use as tracers. Upon finding a satisfactory tracer, the material may be tagged with a radioactive isotope or irradiated to convert stable elements to their radioactive isotopic form to increase the ease and accuracy of detection of the material in minute quantities.

Retention of Oil by Reservoir Rock

Surface Forces in Petroleum Reservoirs

A long-range basic-research program concerned with the nature of the surface forces in various types of petroleum reservoirs has been formulated and prosecuted during the past 3 years. Although there has been no discovery relating to the secret that will unlock the bonds that hold the heretofore unrecoverable oil in place, basic data have been accumulated, which will be necessary for applied research to carry on and make an important discovery. The program is broad in its scope and aims and will continue to coordinate information in several fields of science and technology that bear on these complex phenomena.

Fluid-Flow Phenomena

Studies of single-phase liquid permeability have been made using pure water and various pure hydrocarbon and other organic liquids flowing through packed, unconsolidated beds of clean, carefully sized, crushed quartz. The theory of a newly developed apparatus for measuring liquid permeability by pressure decline, together with early experimental results, was published.26/ Subsequently, improved experimental techniques have been developed to study the permeation of liquids through beds of clean, sized, packed powders, and comparisons are being made of the permeability of various

26/ Dodd, C. G., Davis, J. W., and Pidgeon, F. D., Measurement of Specific Surface Areas of Nonporous Powders by a Pressure-Decline Liquid-Permeability Method: Jour. Phys. and Colloid Chem., vol. 55, No. 5, May 1951, pp. 684-698.

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liquids flowing through beds of the same powder. Specific surface areas of powder samples are calculated from permeability data, and these calculated areas are compared with areas measured by independent methods, such as microscopy and gas adsorption. Thus, surface areas are used as a control in the study of surface effects during permeation, and the amount of immobile liquid in pores, not participating in flow, is estimated. The improved all-glass liquid-permeability apparatus is shown in its thermostatically controlled air bath in figure 8.

Gas-adsorption equipment has been constructed to measure the specific surface areas of powders by the low-temperature adsorption of nitrogen and to determine energies of adsorption of vapors on solids. Precise microscopic methods for measuring particle specific surface have been developed, which constitute a great improvement over previous methods with respect to speed and precision.

The effect of electrokinetic phenomena on flow is being studied in an effort to evaluate their significance, and a paper[27/] was prepared describing the theory on which this work is based. An improved experimental technique has been developed to evaluate the blocking effect of streaming potential when liquids flow through porous mediums. The electrokinetic measurements are made in glass cells similar to those used in the pressure-decline permeability work (fig. 8).

Interfacial Tension Studies

An improved pendent-drop interfacial-tension apparatus was constructed and set up in a vibration-free position in a basement laboratory. Preliminary studies were made of the accuracy and precision of this most suitable method for measuring interfacial tension-aging properties of colloidal systems. The air bath with thermostatic control, optical glass cell, drop-control mechanism, and part of the optical system are shown in figure 9.

Film-Forming Substances

The isolation and analysis of complex substances in petroleum that may be removed by adsorption at an oil-water interface have been studied intensively. The first work was done with a sample of crude petroleum from the Wilcox sand in the Oklahoma City field. Results of microanalyses[28/] indicated a predominance of insoluble, high-melting, giant, long-chain n-paraffins. Traces of metals were found also, but they remained unidentified. Subsequently, larger amounts of the extractives have been isolated from crude petroleum produced in the Rio Bravo, Calif., field. Improved chromatographic adsorption column techniques on a micro scale have been developed to purify the complex extractive mixtures. The metallic elements in the extracts have been correlated with their surface-active and film-forming properties. Pendent-drop interfacial tension-aging studies have been used to determine the activity of each fraction. A newly completed arc-emission spectroscope was used to identify titanium, zinc, calcium, and magnesium in the highly surface-active fractions. Smaller amounts of the same metals plus others such as vanadium and iron together with waxes and resins were found in the film-forming fractions. The metal-carrying constituents are being studied with respect to: (1) The colloidal nature of

27/ Lorenz, P. B., The Phenomenology of Streaming Potential and Electro-Osmosis: Presd. at 119th Meeting, Am. Chem. Soc., Boston, Mass., April 1951.

28/ Denekas, M. O., Carlson, F. T., Moore, J. W., and Dodd, C. G., Materials Adsorbed at Crude Petroleum-Water Interfaces. Isolation and Analysis of Normal Paraffins of High Molecular Weight: Ind. Eng. Chem., vol. 43, 1952, p. 1165.

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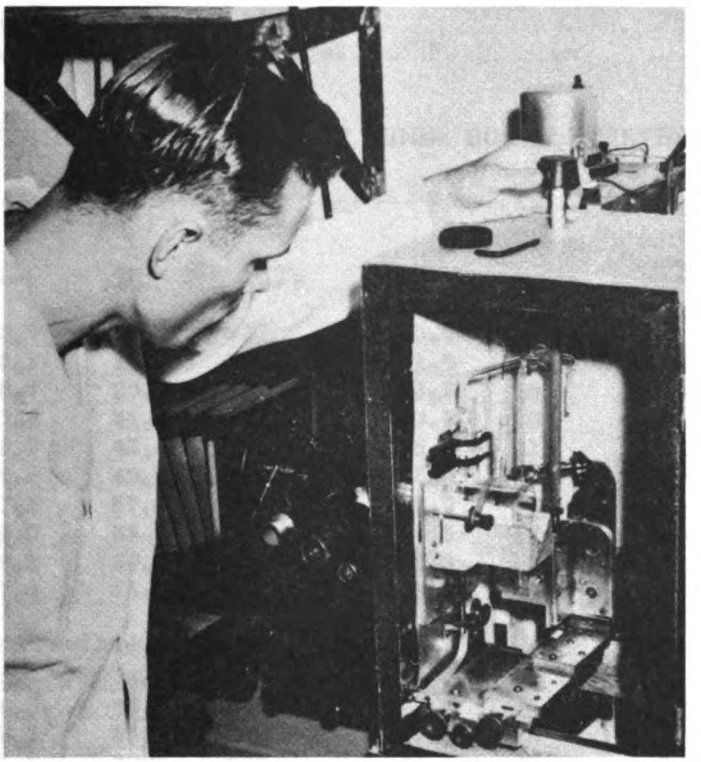

Figure 9. - Pendent-drop interfacial-tension apparatus showing thermostatically controlled air bath, optical-glass cell, drop-control mechanism, and part of the optical system.

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6-425
(January 1949)

REPORT OF CRUDE PETROLEUM ANALYSIS

Bureau of Mines Laramie Laboratory
Sample PC-51-165

IDENTIFICATION

Beaver Lodge field
Devonian (Jefferson) limestone
11,630 - 11,660 feet

North Dakota
Williams County
C SW 1/4 SW 1/4 sec. 6,
T. 155 N., R. 95 W.

GENERAL CHARACTERISTICS

Specific gravity, 0.767 A. P. I. gravity 53.0° Pour point, ° F. below 5
Sulfur, percent, less than 0.10 less than Color, NPA 4
Saybolt Universal viscosity at 100° F., 32 sec.; at ° F., sec.

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 760 mm. Hg.
First drop, 23° C. (73 ° F.)

Fraction No.	Cut at ° C.	Cut at ° F.	Percent	Sum, Percent	Sp. Gr., 60/60° F.	° A. P. I., 60° F.	C. I.	Aniline Point, ° C.	S. U. Visc., 100° F.	Cloud Test, ° F.
1	50	122	5.9	5.9	0.637	90.6				
2	75	167	6.1	12.0	664	81.6	4.6	56.0		
3	100	212	8.7	20.7	706	68.9	15	56.0		
4	125	257	10.8	31.5	736	60.8	20	51.0		
5	150	302	9.5	41.0	755	55.9	21	50.7		
6	175	347	8.5	49.5	767	53.0	20	55.8		
7	200	392	7.5	57.0	776	50.9	18	63.6		
8	225	437	6.0	63.0	786	48.5	17	69.6		
9	250	482	6.5	69.5	799	45.6	18	74.1		
10	275	527	7.0	76.5	811	43.0	19	78.8		

STAGE 2—Distillation continued at 40 mm. Hg.

11	200	392	2.2	78.7	0.826	39.8	22	82.1	38	25
12	225	437	4.3	83.0	831	38.8	21	86.1	41	40
13	250	482	3.7	86.7	840	37.0	22	90.9	48	60
14	275	527	2.8	89.5	852	34.6	24	96.0	59	75
15	300	572	3.5	93.0	860	33.0	25	101.0	83	90
Residuum			6.3	99.3	898	26.1		114.5		

Carbon residue of residuum, 1.4 percent; carbon residue of crude, .1 percent.

APPROXIMATE SUMMARY

	Percent	Sp. Gr.	° A. P. I.	Viscosity
Light gasoline	20.7	0.674	78.4	
Total gasoline and naphtha	57.0	0.727	63.1	
Kerosine distillate	19.5	799	45.6	
Gas oil	9.0	853	34.4	
Nonviscous lubricating distillate	7.5	843-865	36.1-32.1	50–100
Medium lubricating distillate	.0			100–200
Viscous lubricating distillate	.0			Above 200
Residuum	6.3	898	26.1	
Distillation loss	.7			

Figure 10.

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petroleum; (2) the preferential wetting of petroleum reservoir rocks by oil, and the study of core samples in the laboratory; (3) the biogenesis of petroleum; (4) the analysis of petroleum for trace metallic constituents; and (5) the development of methods for removing undesirable metals from petroleum.

PETROLEUM CHEMISTRY AND REFINING

During the past several years, chemistry and refining research has been guided by a program designed to provide basic information on the relationships of the composition of petroleum products and their utilization. From time to time, some of the projects under this program have been completed or new ones added, but a review of previous annual reports shows consistent progress in the direction of the program objectives. However, as the utilization of petroleum products is in continual evolution and is always creating new problems for solution, ultimate attainment of a final objective of the program is only theoretically possible.

The program defining the research work can be identified conveniently by the following titles, used to caption the pertaining discussions:

1. Crude-oil analysis.
2. Sulfur compounds in petroleum.
3. Composition of fuel in relation to utilization characteristics.
4. Composition and properties of asphalts.
5. Fuel surveys.

Crude-Oil Analysis

Routine-Type Analyses

During the year 244 crude-oil samples from domestic and foreign fields were analyzed by the Bureau of Mines routine method. Geographical distribution of the samples was as follows:

California 12, Colorado 10, Kansas 3, Louisiana 6, Montana 24, Nebraska 3, North Dakota 1, Oklahoma 51, Pennsylvania 18, Texas 21, Utah 4, Wyoming 82. Alaska 5, Canada 3, and Netherlands East Indies 1.

Among the oils analyzed was a sample from the first well in North Dakota (fig. 10). This well not only added North Dakota to the list of oil-producing States but also opened the Williston Basin to more thorough exploration.

Several reports were prepared regarding crude-oil analyses. These included parts III, IV, and V[29] of a series of reports regarding refining properties of new

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29/ Ball, John S., Wenger, W. J., and Whisman, M. L., Refining Properties of New Crudes: Part III - Oil from 20 New Discoveries in Rocky Mountain Region Analyzed: Petrol. Processing, vol. 5, No. 8, August 1950, pp. 842-846. Smith, N. A. C., Smith, H. M., and McKinney, C. M., Refining Properties of New Crudes: Part IV - Crude Oils from Recent Discoveries in Kansas: Petrol. Processing, vol. 5, No. 9, September 1950, pp. 960-964. Part V - Crude Oils from the "Golden Trend" in Oklahoma: Petrol. Processing (in press).

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crude oils published in Petroleum Processing. Parts I and II of this series were cited in the annual report for 1950. A summary of analytical data on United States crude oils of importance during the period 1935-45, with data on the characteristics of light naphthas from several of them, was published in the new volume of The Science of Petroleum.30/

A report31/ describing in detail the methods and equipment used in the Bureau of Mines routine crude-oil analysis was published during the year. This publication satisfies a long-felt desire for an adequate and concise description of the Bureau's crude-oil analysis work, and there has been a wide demand for copies.

The large number of analyses of routine type now available, together with recent data providing increased information regarding the characteristics of the fractions obtained, has made it possible to make a statistical study of crude oils from several viewpoints. At present the following properties and characteristics have been examined: Viscosity; contents of sulfur; asphalt; naphtha and gas oil; and the contents of aromatics, paraffins plus naphthenes, and percent of naphthene ring in the paraffin-naphthene portion of both naphthas and gas oils. The results of these studies were reported in several papers.32/

Sulfur Compounds in Petroleum

Work under American Petroleum Institute Research Project 48A on the Production, Isolation, and Purification of Sulfur Compounds and Measurement of their Properties, as in past years, is separated into three independent but related phases. They are:

1. Synthesis, purification, and determination of properties of sulfur compounds.

2. Separation, isolation, and identification of sulfur compounds in crude oils.

3. Determination of thermodynamic data of sulfur compounds.

The first two phases of this project are being carried out at Laramie, Wyo., and Bartlesville, Okla., respectively, and are discussed below. The third phase is being conducted at Bartlesville and is discussed under a later section on thermodynamics of petroleum.

30/ Smith, H. M., The Crude Oils of the U. S. A., 1934-45: Science of Petrol., vol. 5, Oxford Press, New York, 1950, pp. 3-20.

31/ Smith, N. A. C., Smith, H. M., Blade, O. C., and Garton, E. L., The Bureau of Mines Routine Method for the Analysis of Crude Petroleum, I. The Analytical Method: Bureau of Mines Bull. 490, 1951, 82 pp.

32/ Smith, Harold M., Composition of United States Crude Oils: Pres. at the Symposium on Composition of Crude Oil before the Petroleum Chemistry Div., Am. Chem. Soc., Cleveland, April 9, 1951. In press. Characteristics of Crude Oils Currently Produced in the United States: Oil and Gas Jour., vol. 49, No. 47, Mar. 29, 1951, pp. 308-317. Composition of United States and Some Foreign Crude Oils: Proc. 3d World Petroleum Congress, The Hague, Netherlands, sec. 6, 1951, pp. 319-335.

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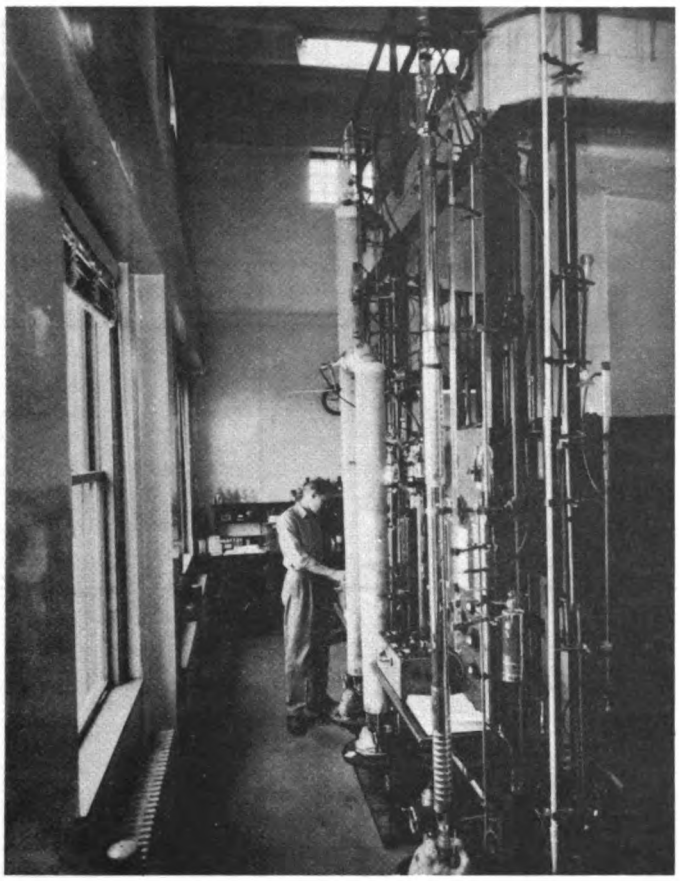

Figure 11. - Efficient distillation columns are used in purifying sulfur compounds for calibration standards.

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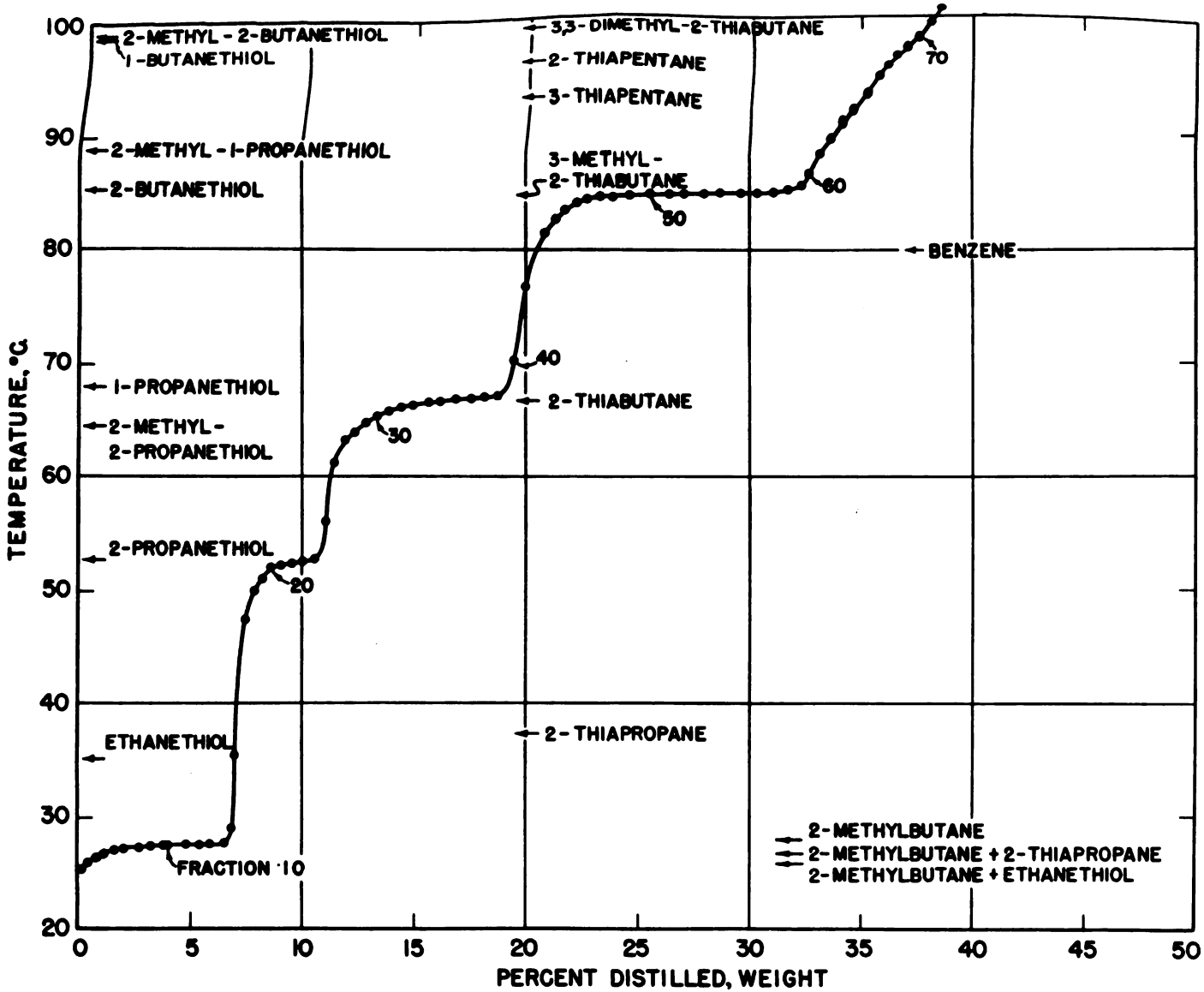

Figure 12. - Fractionation of sulfur concentrate from Wasson distillate.

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Synthesis, Purification, and Determination of Properties of Sulfur Compounds

The program to determine physical properties of the sulfur compounds in petroleum requires the use of highly purified samples. Consequently, the Bureau of Mines, in cooperation with the American Petroleum Institute, is actively engaged in the synthesis and purifications of sulfur compounds (see fig. 11) as well as the determination of properties. This cooperative effort resulted in the production of four additional pure sulfur compounds during the past year. These compounds are 3-methylthiophene, 1-butanethiol, 2-thiapropane (dimethyl sulfide), and 2,3-benzothiophene. These join the list of 11 compounds previously purified. Precise measurements of purity, freezing point, boiling point, refractive index, density, surface tension, and viscosity have been completed on 14 of the compounds. Ultraviolet, infrared, and mass spectra have been determined for 10 of the compounds. The purified compounds are used also in determining thermodynamic properties and comparing standards in separating and identifying sulfur compounds from petroleum.

In purifying the sulfur compounds, more material than that needed for the work of the Bureau is prepared. This additional material is made available to industrial and educational laboratories for calibration of spectrometers at $35 per 5 ml. The first eight compounds were packaged and are being sold by the National Bureau of Standards. A change in policy this year resulted in the packaging being done at the Bureau of Mines and the sales being made through the American Petroleum Institute.

Compilation and correlation of reported work on sulfur compounds has continued. The tables of physical properties, as selected from the literature reports, have been brought up to date, anticipating publication. The literature has been reviewed as to the present knowledge of the sulfur compounds present in petroleum and two papers presented.33/34/

Separation and Identification

Work of the previous year on the types of sulfur compounds in straight-run naphthas from 17 crude oils was published.35/

During 1950-51 the project has identified, in a distillate from Wasson crude oil, the sulfur compounds boiling below 95° C. A concentrate was separated from the crude oil containing essentially nothing except sulfur compounds, with only trace contamination of benzene and some isopentane used in the concentrating procedure. Fractionation of this concentrate, as shown in figure 12, with subsequent analysis by infrared absorption of the fractions obtained, led to the identification of every theoretically possible mercaptan and aliphatic sulfide in the distillate boiling up to 95° C., including three not previously reported as present in petroleum. No traces of carbon disulfide, thiophene, or cyclic sulfides were found. One compound, 2-methyl-2-butanethiol, boiling above 95° C. also was identified.

The procedure used has four essential steps: (1) Separation of a distillate from main portion of crude oil; (2) separation of sulfur compounds from the distillate by percolation through alumina; (3) fractionation of sulfur concentrates so

33/ Ball, J. S., Waddington, G., Rall, H. T., and Smith, H. M., Sulfur Compounds of Petroleum: Pres. at Am. Chem. Soc. meeting, Cleveland, Ohio, Apr. 9, 1951.

34/ Ball, John S., Sulfur Compounds in Petroleum: Pres. at Gordon Research Conference, New London, N. H., June 29, 1951.

35/ Hale, J. H., Thompson, C. J., Barker, M. G., Smith, H. M., and Ball, J. S., Distribution and Type of Sulfur Compounds in Straight-Run Naphthas: Anal. Chem., vol. 23, 1951, pp. 287-293.

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obtained in semimicro apparatus; (4) analysis of fractions for individual compounds. The first step or primary distillation was a continuous isothermal (steam-heated) procedure that provided a naphtha containing all sulfur compounds within a selected boiling range without subjecting the crude oil to a temperature higher than 100° C. The entire program of work is outlined in the block diagram, figure 13, which includes percentage-recovery values, based on the crude-oil charge, at various stages of the process. The sulfur compounds in the final blocks were definitely identified by their infrared spectra in the designated fractions. These fractions were the only ones investigated by infrared techniques, and it can be assumed that the sulfur compounds also are present in fractions intermediate to and, to a diminishing extent, on either side of the designated fractions.

Other subordinate problems also have been investigated, including the efficiency of alumina as an absorbent of sulfur compounds and the stability to heat of sulfur compounds in crude petroleum. Much of this work has been described in a paper presented before the American Chemical Society.36/

Thermal Decomposition of Sulfur Compounds

The mechanism of the breakdown of sulfur compounds during thermal treatment is under investigation. Three sulfur compounds - 2-methyl-2-propanethiol, 1-pentanethiol, and thiacyclopentane - have been decomposed under ranges of temperature and residence time that give slight to almost-complete decomposition.

Although ultimately this work is expected to yield valuable results in the interpretation of petroleum reactions, the present work is designated to reduce the complicating factors. Pure compounds are used, so that only the reaction of the sulfur compound - uncomplicated by hydrocarbon reaction products - is studied. The decompositions are carried out in a quartz tube to reduce catalytic effects.

Considerable differences are found in the mechanism of decomposition of 2-methyl-2-propanethiol (t-butyl mercaptan) and 1-pentanethiol (n-amyl mercaptan). The predominant reaction in both instances is to give the corresponding olefin and hydrogen sulfide. However, the 2-methyl-2-butanethiol reaction also gives appreciable quantities of elemental sulfur and tarry materials but the 1-pentanethiol gives neither. A free radical mechanism has been advanced to explain the decomposition of the 2-methyl-2-butanethiol.

Nitrogen Compounds in Petroleum

Although the presence of nitrogen compounds in crude oils has a detrimental effect on refining properties, little information has been available concerning the amount of nitrogen in various crude oils. To supply this needed information a survey was made of 153 crude petroleums from 17 States and 3 foreign countries. The report37/ of this work also indicates how nitrogen contents may be estimated from the carbon residue of the crude oil, knowing the geological formation from which it was produced.

36/ Ball, J. S., Rall, H. T., Waddington, Guy, and Smith, H. M., Sulfur Compounds in Petroleum: Pres. before Petroleum Division, Am. Chem. Soc., Cleveland, Apr. 9, 1951. In press.

37/ Ball, John S., Whisman, M. L., and Wenger, W. J., Nitrogen Content of Crude Petroleums: Ind. Eng. Chem. In press.

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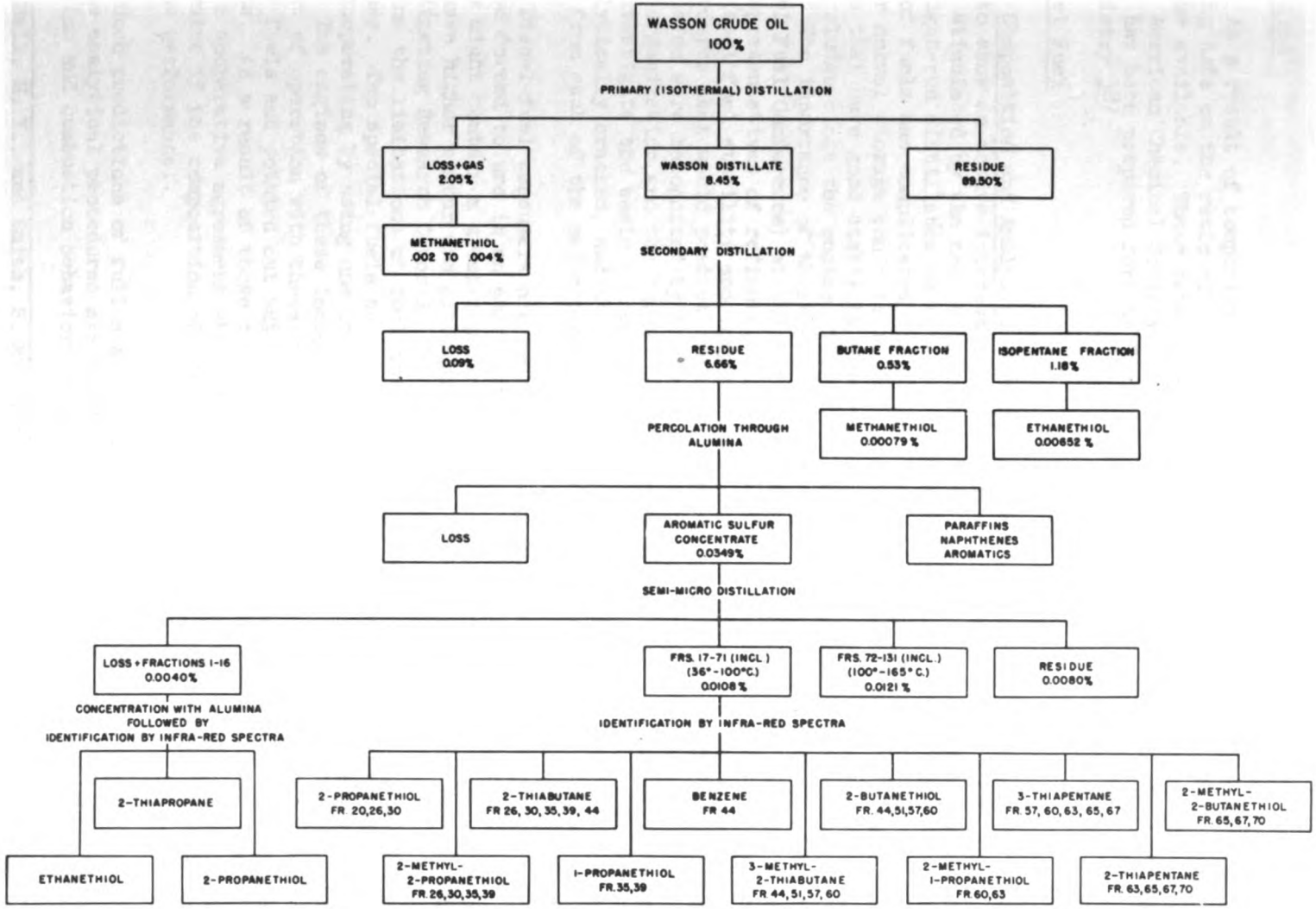

Figure 13. - Separation of individual sulfur compounds.

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Composition of Fuels and Utilization Characteristics

Gasoline

As a result of composition studies on gasoline during the last decade, interesting data on the ratio of the content of various hydrocarbons in crude oils has become available. These data were presented at the Fourth Oklahoma Trisection Meeting, American Chemical Society, in Bartlesville in October 1950, and a revised version has been prepared for the International Congress of Pure and Applied Chemistry.38/

Diesel Fuel

Composition and Analysis. - Petroleum refiners and engine builders have continued to show an active interest in the quality of Diesel fuels. Their interest has been stimulated by the necessity of blending catalytically cracked stocks with straight-run distillates to meet the increased demand for Diesel fuels. This blending of fuels has complicated the storage problem, because these fuels deteriorate under normal storage conditions. It also has been found that, in some cases, two fuels that have good stability when stored separately will cause a sludge when mixed. This sludge clogs the engine filters and injector nozzles, which causes engine failure. The importance of these problems was emphasized at a conference (Fifth Annual Diesel Fuel Conference) at the Bartlesville Petroleum Experiment Station. A panel of representatives of refiners, engine builders, and consumers discussed the problem of Diesel fuel stability and compatibility and emphasized the need for devising test procedures that would predict the stability and compatibility of fuels. These problems also were recognized by the Western Petroleum Refiners Association (WPRA). That organization and the Bureau of Mines have entered into a cooperative agreement to investigate the basic causes of the stability and compatibility of straight-run, catalytically cracked, and thermally cracked distillates from representative crude oils from each of the major producing areas of the country.

Diesel-fuel consumers are concerned about the quality of Diesel fuel that they may be forced to use in an emergency. Fuels that would be available during an emergency might contain a greater percentage of cracked stock, have a higher end point, and have higher sulfur and nitrogen contents. To anticipate this possibility, the Coordinating Research Council (CRC) is sponsoring full-scale railroad tests to determine the limitations of fuel that can be burned successfully in railroad Diesel engines. Ten special fuels have been made by refiners, and several of the railroads are cooperating by using one of these fuels exclusively in a locomotive on a regular run. The engines of these locomotives are inspected periodically to determine the effect of operation with these special fuels. The Bureau of Mines analyzed two of these fuels and pointed out why one of them might have caused excessive engine deposits. As a result of these tests, the CRC and the Bureau of Mines have entered into a cooperative agreement whereby the Bureau will analyze each of the fuels to determine if the composition of the fuel can be correlated with full-scale railroad-engine performance.

Such predictions of full-scale engine performance of fuels from comparatively simple analytical procedures are possible only because of correlations between composition and combustion behavior developed during more comprehensive studies of

38/ Rall, H. T., and Smith, H. M., Composition of Petroleum: Relationship of Hydrocarbon Types Through C_6-C_9 Hydrocarbons: To be pres. at 12th Cong. of Pure and Applied Chemistry, New York, September 1951.

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representative types of fuels. These comprehensive studies were conducted in cooperation with the WPRA and the Navy. The WPRA program involves the study of Diesel fuels prepared from several selected crude oils that are representative of large production. The first fuel selected was prepared from West Edmond, Okla., crude oil,[39][40] a representative Midcontinent oil. The Diesel-fuel cut first was fractionated, and then each fraction was separated into a paraffin-naphthene and an aromatic portion by percolation through silica gel. The original fraction and each of the portions were studied separately. The next fuel chosen was prepared from Hastings, Tex., crude oil, which is typical of Gulf coast production. This Diesel fuel is being separated into a paraffin-naphthene portion and an aromatic portion; each portion will be fractionated separately. Aromatics were removed before fractionating because experience with the West Edmond fuel showed that the aromatics azeotroped with the other hydrocarbons, causing them to boil at other than their true boiling points, and resulted in poorer fractionation. The results of cooperative work with the WPRA were presented at that organization's annual meeting.[41]

The Bureau analyzed a catalytically cracked fuel and a Fischer-Tropsch fuel[42] as a part of the Navy program.

The development and refinement of separation techniques are being conducted concurrently with the composition studies. One separation technique being investigated is that of liquid thermal diffusion. Both static and continuous columns have been constructed to test the feasibility of separating the paraffin- and naphthene-type hydrocarbons.

The primary separation process in the Diesel-fuel studies, as well as most other petroleum research, is fractionation, and in order to utilize this tool better a 5-gallon stainless-steel experimental still was designed and constructed. This still will be used to evaluate and determine the limitations of different types of random packing.

In connection with the study of Diesel fuel composition, the infrared spectra of six C_{14} hydrocarbons were examined for differences and similarities in spectra caused by progressive change in structure from a chain compound (C_6H_{13})-CH_2-CH_2-(C_6H_{13}) to those where there was complete replacement of the (C_6H_{13}) group by a cyclohexane or benzene ring.[43] This study was in cooperation with Dr. J. Rud Nielsen of the University of Oklahoma.

39/ Schwartz, F. G., Hopkins, R. L., and Coleman, H. J., Composition of Naphthas and Gas Oil from West Edmond, Okla. Crude Oil: 4th Oklahoma Trisectional Meeting, Am. Chem. Soc., Bartlesville, Okla., Oct. 21, 1950.

40/ Adams, Norman G., and Richardson, Dorothy M., Aromatic Hydrocarbons in Some Diesel-Fuel Fractions: Anal. Chem., vol. 23, 1951, pp. 129-133.

41/ Ward, C. C., and Smith, H. M., Why Diesel Fuels Behave as They Do: Western Petrol. Refiners Assoc., 39th Ann. Meeting, San Antonio, Tex., Apr. 2-4, 1951.

42/ Ward, C. C., Schwartz, F. G., and Adams, N. G., Composition of Fischer-Tropsch Diesel Fuel (Cobalt Catalyst): Ind. Eng. Chem., vol. 43, 1951, p. 1117.

43/ Adams, N. G , and Nielsen, J. Rud, The Infrared Absorption Spectra of Six C_{14} Hydrocarbons and Their Application to the Study of Diesel Fuels: Proc. Oklahoma Acad. Science, vol. 30, 1951, pp. 154-166.

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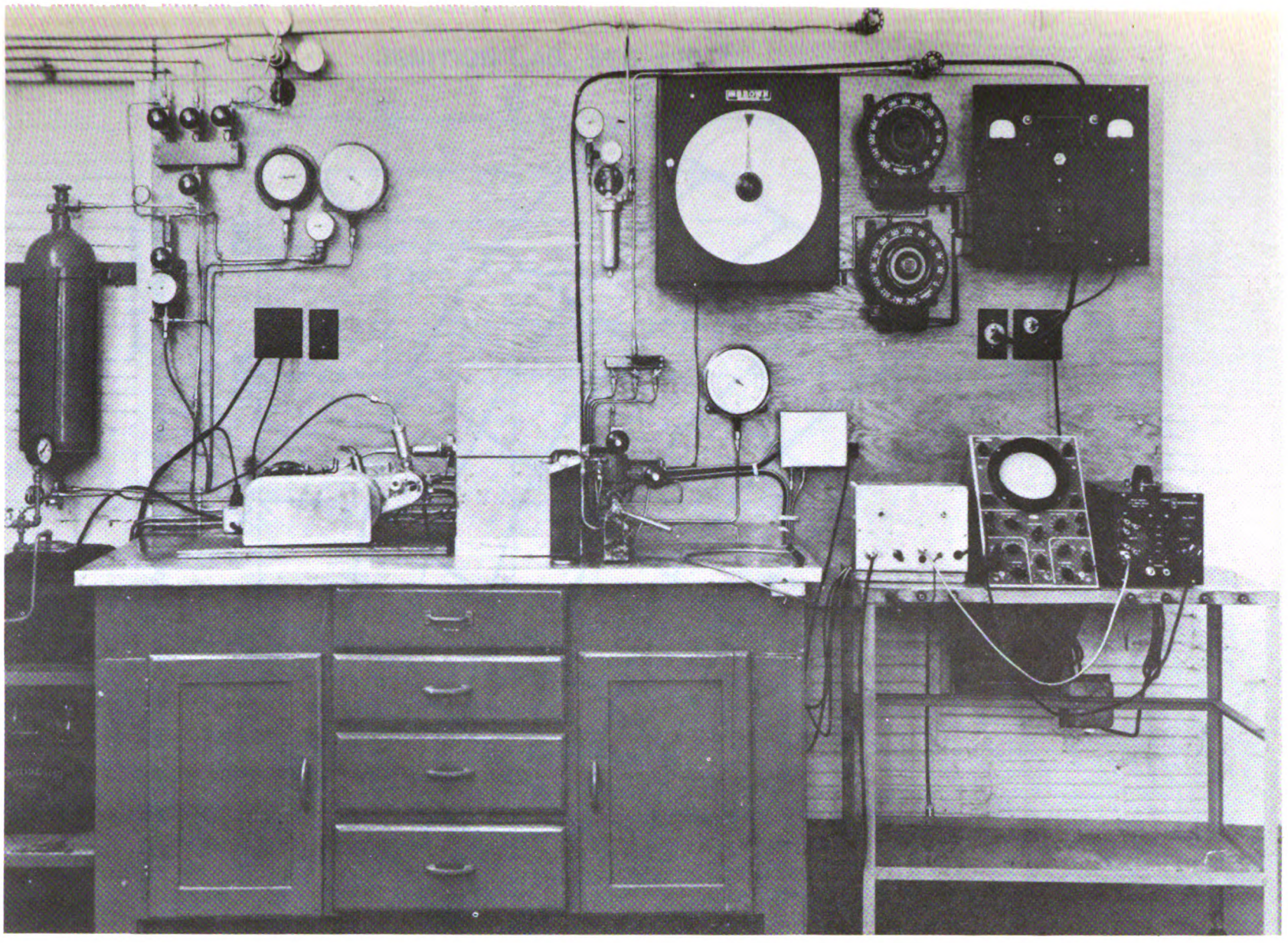

Figure 14. - Constant-volume combustion bomb and accessories.

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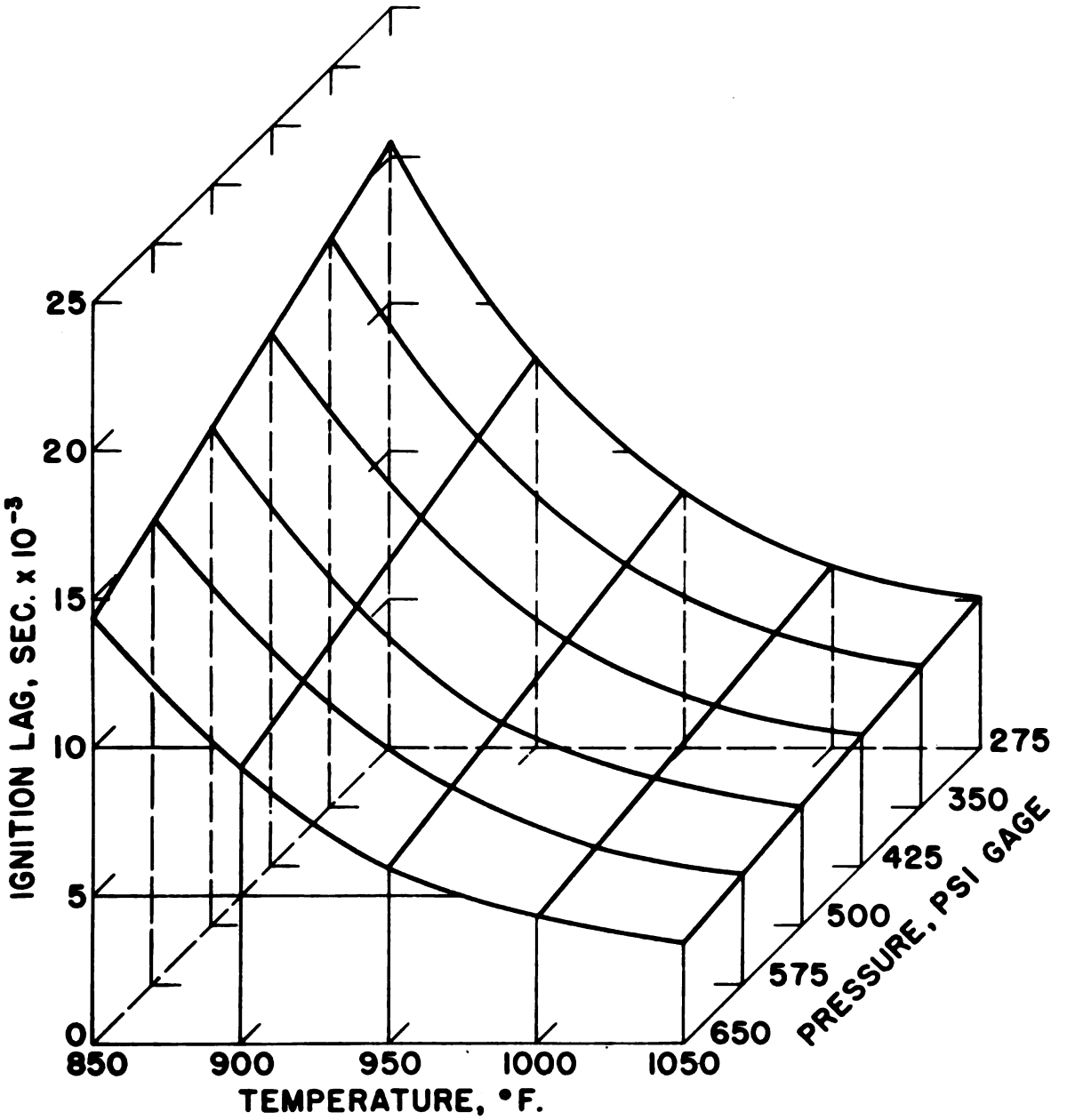

Figure 15. - Typical ignition characteristics as obtained from the constant-volume combustion bomb.

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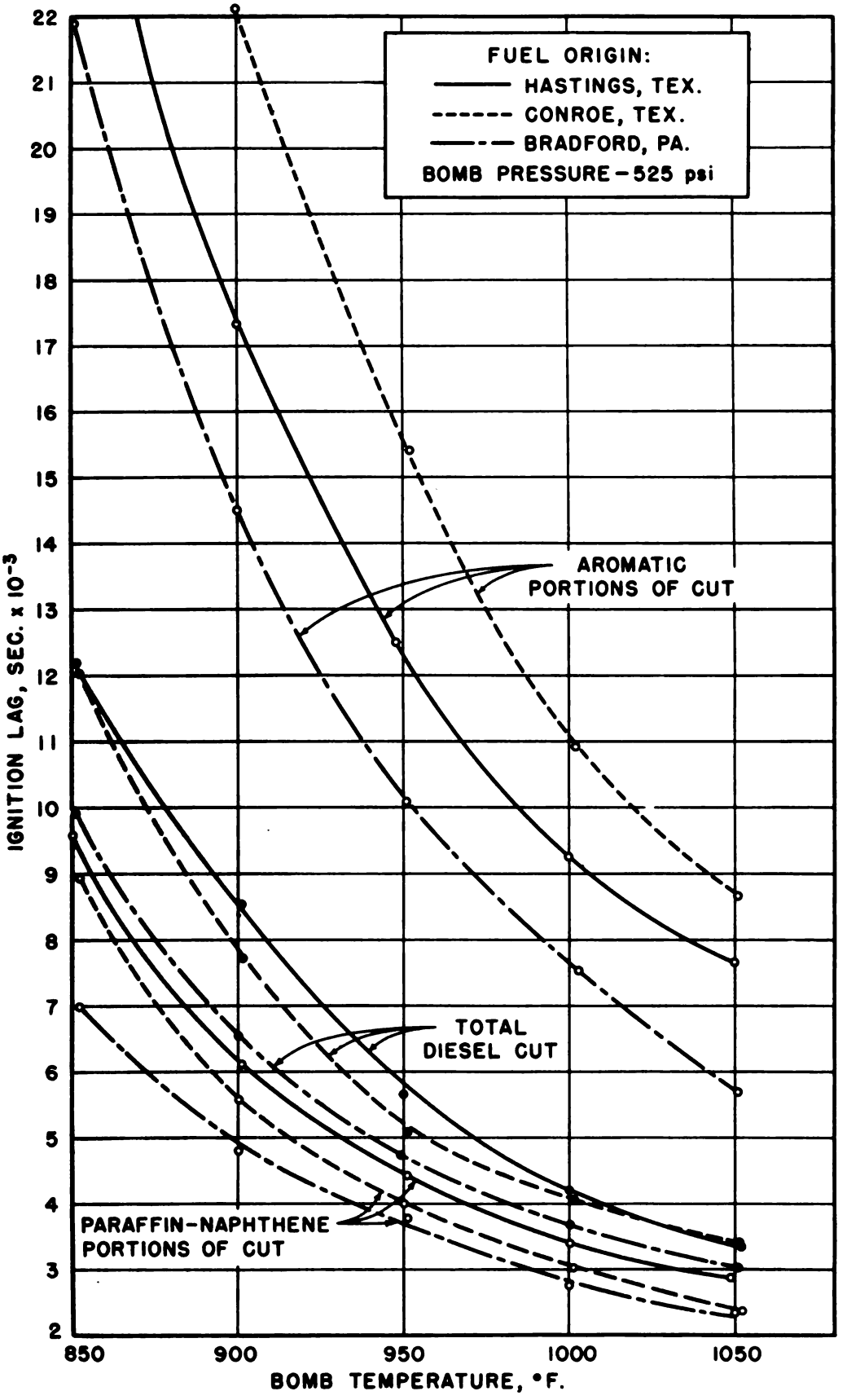

Figure 16. - Bomb data, showing influence of hydrocarbon type on ignition characteristics.

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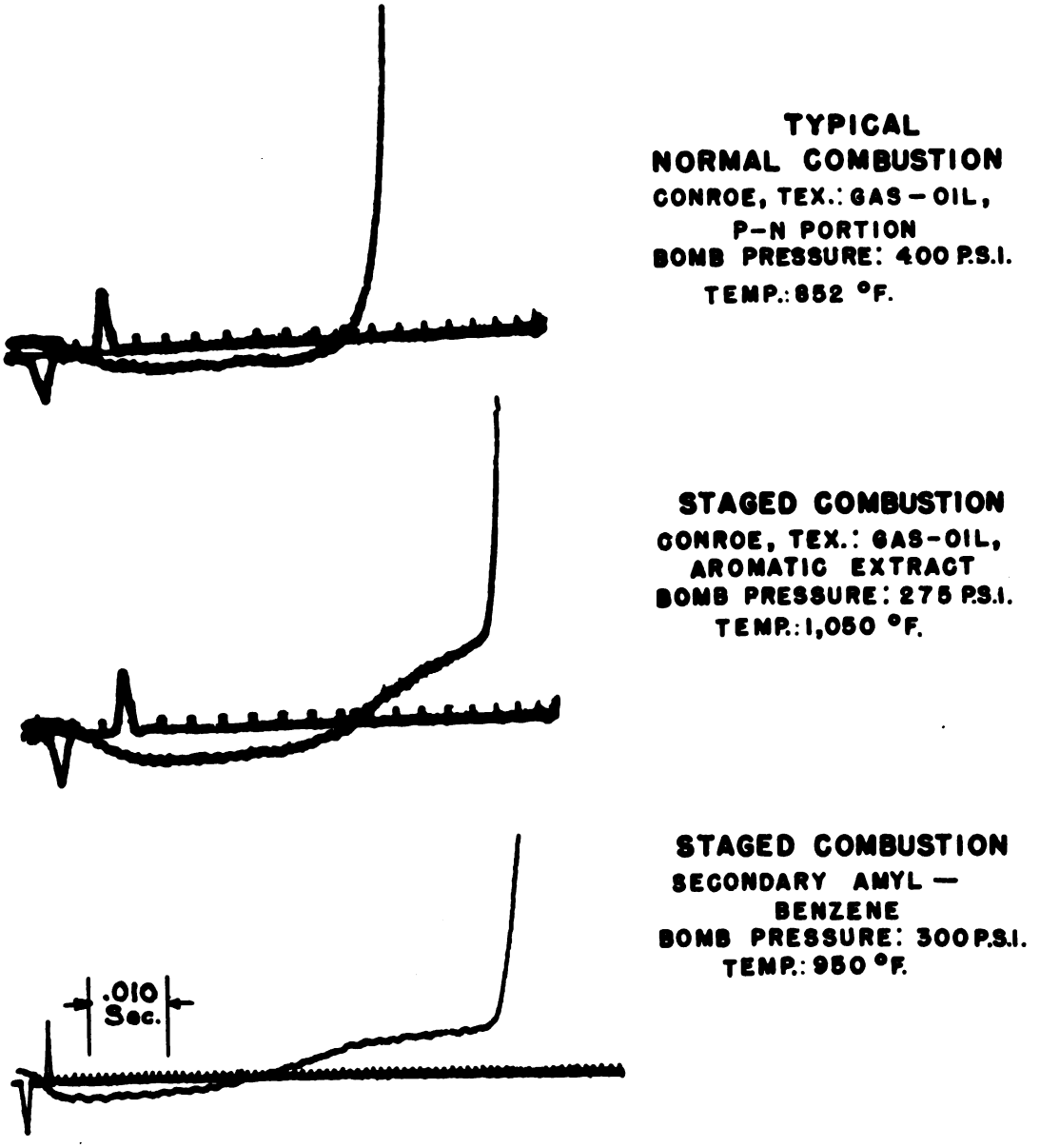

Figure 17. - Variations in combustion-pressure development in constant-volume combustion bomb. (Timing marks - 1 millisecond).

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One of the laboratory devices used in studying the large number of Diesel-fuel fractions mentioned above was a continuous solvent stripper used at the effluent end of the silica-gel percolation column.[44]

Determination of properties is always important in any study of composition; and, in conjunction with the study of cyclo-octatetraene by the thermodynamics group, this compound was purified and several properties determined.[45]

Cooperative work on methods for the determination of density were completed and reported.[46]

Utilization. - Researches on utilization were directed primarily toward combustion research on commercial-type Diesel fuels, the component fractions of commercial-type fuels, and pure hydrocarbons in the range C_{10} to C_{32}. Major emphasis was placed on investigations that sought to establish relationships between the composition of a fuel and its ignition and combustion characteristics over wide ranges of ignition pressures and temperatures. Exploratory studies were made of the effects of fuel-injection variables on the ignition-combustion characteristics.

Combustion Studies with Constant-Volume Bomb. - The technique in the use of the constant-volume combustion bomb for the study of fuel-combustion properties was not changed, but important refinements of instrumentation were made in the accessory apparatus. These developments made it possible to attain reproducible results in these combustion studies. A picture of the complete set-up is shown in figure 14.

The good reproducibility, flexibility of control, and small sample requirement of this apparatus have made it possible to chart ignition characteristics of fuels over the complete range of pressures and temperatures, which may assist in predicting fuels characteristic in engine operation. Such a chart is shown in figure 15.

Data obtained from tests of fuels in this equipment were used to evaluate the combustion characteristics of the component portions of Diesel fuels and to determine how these component fractions affect the ignition and combustion characteristics of the composite fuel. Figure 16 illustrates these data obtained on three fuels of distinctly different characteristics. Of even greater interest from a fundamental standpoint, the bomb data were studied to analyze their significance in relation to the mechanisms by which combustion proceeds. Figure 17 illustrates data that are of particular interest in these studies.

A general discussion of the constant-volume combustion-bomb experiments and results of tests on several fuels were presented to the Society of Automotive Engineers at its annual meeting in Detroit in January.[47] Additional data obtained on tests of pure hydrocarbons were presented to the American Chemical Society meeting in Cleveland in April.[48]

44/ Hopkins, R. L., Continuous Stripper for Adsorption Column Effluent Streams: Ind. Eng. Chem., vol. 43, 1951, pp. 1456-1458.

45/ Eccleston, B. H., Coleman, H. J., and Adams, N. G., The Purification and Some Physical Properties of Cyclooctatetraene: Jour. Am. Chem. Soc., vol. 72, 1950, pp. 3866-3870.

46/ Smith, H. M., and Cooperators, Measurement of Density of Hydrocarbon Liquids by the Pycnometer: Anal. Chem., vol. 22, 1950, pp. 1452-1453.

47/ Hurn, R. W , and Hughes, K. J., Combustion Characteristics of Diesel Fuels as Measured in a Constant-Volume Bomb: Pres. before Soc. Auto. Eng., Ann. Meeting, Jan. 8, 1951, Detroit, Mich.

48/ Hurn, R. W., and Smith, H. M., Combustion Studies of Hydrocarbons in the Diesel Fuel Boiling Range: Pres. before Petroleum Chemistry Div., Am. Chem. Soc., Cleveland, Apr. 11, 1951.

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The Internal Combustion Engine Institute indicated its interest in these studies and joined the A.P.I. in sponsoring a portion of the program being conducted in cooperation with the Coordinating Research Council. Other industry and military representatives continued to exhibit a marked interest in the work.

Fuel Testing by Engine

Fundamental studies of combustion in full-scale single-cylinder engines were largely curtailed during the year because of emphasis on development of the constant-volume combustion-bomb equipment. Some additional work was done on instrumentation of a Diesel test engine, and preparations were made for installing a special research unit that will allow engine tests over wide ranges of load and speed conditions.

The personnel of the engine laboratory remained active in local and national fuel-testing activities pertaining to motor-gasoline and Diesel-fuel samples, including those processed by the laboratory and exchange samples used to test rating precision. This work kept them abreast of new developments and utilized the facilities of the laboratory in the refinement of techniques and apparatus for fuel testing.

Fuel Surveys

Three reports appeared during the fiscal year giving the results of two surveys of motor gasoline.[49/][50/][51/] There was one survey of aviation gasoline[52/][53/] and one survey of Diesel fuel.[54/][55/]

These surveys are conducted under a cooperative agreement between the United States Department of the Interior, Bureau of Mines, and the American Petroleum Institute. Under the agreement, samples of the fuels are analyzed in the laboratories of oil, chemical, and motor companies by standard procedures and the results submitted to the Bureau of Mines for compilation and publication. The reports are in demand by refiners of petroleum, chemical and motor manufacturers and by consumers who need information on the properties of motor and aviation gasolines and Diesel fuels.

The motor-gasoline surveys of summer 1950 and winter 1950-51 showed that octane numbers of automobile fuels rose sharply to establish new record values. As the following tabulation shows, the national-average octane ratings by both research and motor methods are one octane unit above those for the preceding winter and one and one-half to two units higher than the ratings of the summer of 1949.

49/ Blade, O. C., National Motor-Gasoline Survey, Summer 1950: Bureau of Mines Rept. of Investigations 4765, 1950, 33 pp.

50/ Blade, O. C., National Motor-Gasoline Survey, Winter 1950-51: Bureau of Mines Rept. of Investigations 4809, 1951, 34 pp.

51/ Blade, O. C., Octane Numbers of Gasolines Hit Record Levels Last Summer: Oil and Gas Jour., vol. 48, No. 40, Feb. 9, 1951, p. 99.

52/ Blade, O. C. National Annual Survey of Commercial Aviation Gasoline, October 1950 Production: Bureau of Mines Rept. of Investigations 4789, 1951, 11 pp.

53/ Blade, O. C., National Annual Survey of Commercial Aviation Gasoline: Oil and Gas Jour., vol. 49, No. 50, Apr. 19, 1951, p. 238.

54/ Blade, O. C., National Annual Diesel-Fuel Survey, 1950: Bureau of Mines Rept. of Investigations 4746, 1950, 25 pp.

55/ Blade, O. C., 1950 Diesel-Fuel Survey. Report on 266 Samples Manufactured by 56 Companies: Oil and Gas Jour., vol. 49, No. 34, Dec. 28, 1950, p. 81.

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Grade of gasoline	Fiscal year 1949		Fiscal year 1950		Fiscal year 1951	
	Summer 1948	Winter 1948-49	Summer 1949	Winter 1949-50	Summer 1950	Winter 1950-51
Research octane number:						
Premium price	86.1	86.5	88.0	89.0	90.0	90.3
Regular price	80.1	80.5	81.9	82.4	83.5	83.7
Motor octane number:						
Premium price	79.5	79.7	80.4	81.2	82.0	82.5
Regular price	75.2	75.6	76.4	77.1	78.2	78.8

The first annual survey of Diesel fuels was published in November 1950. Data on 266 samples of Diesel fuel were contributed by 56 refiners for the survey. The analyses, each representing 14 tests, were compiled in two independent arrangements.

The first arrangement was a designation according to type of service: (1) Diesel fuel oils for city buses and similar service; (2) fuels for Diesel engines in trucks, tractors, and similar service; (3) fuel for railroad Diesel engines; and (4) heavy-distillate and residual fuels for large stationary and marine Diesel engines. Data in each class were subdivided to show the analyses of Diesel fuels designated for use only in summer or winter seasons, respectively.

In the second arrangement the data were grouped according to A.S.T.M. grades as follows: (1-D) Diesel fuels of 625° F. maximum end point; (2-D, first section) Diesel fuels of 675° F. maximum 90 percent distillation temperature, with pour points of 0° F. and below; (2-D, second section) Diesel fuels, of same 90 percent temperature, with pour points above 0° F.; and (4-D) Diesel fuels not conforming to the above limitations.

Some Diesel fuels also are marketed as burner fuel oil. The grades of fuel oil indicated by the contributing companies were included in the tabulations. In addition, district numbers were given to indicate the marketing areas as supplied by the manufacturers of the fuels. A map in the report indicates the districts.

Table 1 summarizes some important characteristics of Diesel fuels as revealed by the survey.

Composition and Properties of Asphalts

Much of the confusion concerning differences in asphalts prepared from different crude oils and by different methods of manufacture is due to a lack of knowledge of the hydrocarbons constituting the asphalt. Isolation and identification of these individual hydrocarbons appears impractical, if not impossible, but a knowledge of the types of the hydrocarbon constituents would be of value for evaluating different asphalts. A study was begun to determine the characteristics of fractions consisting of groups of similar hydrocarbons, from a commercial straight-run asphalt prepared from Oregon Basin, Wyo., crude oil. The initial phase of this project - that of separating the asphalt into several fractions in large enough quantity for further fractionation and determination of properties - is in progress. The method of separating 150-gram samples of the asphalt into crude fractions of pentane-insoluble asphaltenes and pentane-soluble petrolenes is similar to that developed previously[56/] for the quantitative analysis of small samples of asphalt.

56/ Hubbard, Rethel L., and Stanfield, K. E., Determination of Asphaltenes, Oils, and Resins in Asphalt: Anal. Chem., vol. 20, 1948, pp. 460-465.

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TABLE 1. - Summary of values, Diesel-fuel survey, 1950

Diesel fuel oil, class	Flash point A.S.T.M. D93 °F.	Viscosity at 100°F. Kinematic A.S.T.M. D445 c.	Sulfur content A.S.T.M. D129 percent	Carbon residue A.S.T.M. D524 on 10 percent residue, percent	Ash A.S.T.M. D482 percent	Cetane number A.S.T.M. D613	Distillation A.S.T.M. D86 or D158 temperature, °F. I.b.p.	percent recovered 10	50	90	End point
A.S.T.M. grade											
1-D											
Average	159	2.27	0.200	0.053	0.001	52.0	369	417	468	532	575
Minimum	120	1.45	.01	.00	.000	35.0	318	345	388	454	477
Maximum	224	3.78	.983	.27	.010	68.1	470	504	547	591	627
2-D 1/											
Average	171	2.92	.326	.081	.002	50.1	380	441	508	593	652
Minimum	136	2.05	.014	.00	.000	36.0	330	396	452	552	628
Maximum	250	4.75	1.95	.44	.020	61.0	474	507	578	654	710
2-D 2/											
Average	185	3.89	.457	.091	.001	50.3	396	471	541	621	677
Minimum	140	2.69	.054	.00	.000	40.5	329	411	517	583	628
Maximum	265	6.03	2.05	.23	.010	64.2	513	569	607	671	726
4-D											
Average	199	13.70	.79	3/ 1.07	.022	39.5	417	510	622	695	759
Minimum	166	2.11	.16	3/ .01	.000	23.0	340	428	468	617	693
Maximum	265	68.5	2.33	3/ 5.53	.18	59.1	483	598	695	791	913

1/ Pour points, 0° F. or below.
2/ Pour points, above 0° F.
3/ on 100-percent sample.

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Some additional experimental work was done regarding the use of anhydrous crystalline alumina as an adsorbent in the constituent analysis of asphalt. These results agreed with those reported last year in that different lots of alumina may have different adsorption characteristics. Therefore, the same lot of alumina adsorbent should be used to compare constituent analyses of series of different asphalts. The properties of bitumens from bituminous sandstones from the Vernal and Sunnyside deposits in Utah were determined also. Except for low sulfur content - 0.37 to 0.50 percent - these bitumens generally resembled bitumens from other deposits such as those from Edna, Calif., and Athabasca, Canada.

Oils from Near-Surface Deposits

Possible utilization of oils from near-surface deposits in the Uinta Basin of Utah was studied. Samples of bitumen from the Sunnyside and Vernal deposits were separated by the hot-water process at the Bureau of Mines San Francisco laboratory. Data were obtained on the yield and quality of asphalts that could be produced. These asphalts appear to be satisfactory for uses such as road building. The bitumens are deficient in low-boiling constituents but can be used for heavy fuel oil. After a coking distillation, a liquid is obtained that yields gasoline, Diesel fuel, and fuel oil.

Chemicals from Natural Gas

Although most of the Bureau's studies on petroleum utilization have been devoted to liquid hydrocarbons and their derivatives, the Bureau also has followed current developments in the utilization of natural gas, and some of the developments in this field were reported at a conference on gas technology.57/

THERMODYNAMICS OF PETROLEUM

The Bureau of Mines has long recognized the importance of thermodynamic data to the chemical industry in both peace and war and, to provide such data, has maintained a well-equipped thermodynamic laboratory at Bartlesville, Okla. The facilities of this laboratory are utilized for measurement of fundamental properties of hydrocarbons and related substances. During the past year, many research investigations have been completed or initiated, and the results of the completed studies have been published promptly in scientific journals or otherwise made available to the industries that have vital need for the new information obtained.

One comprehensive program of particular interest, carried out in cooperation with the American Petroleum Institute, has made particularly good progress during the past year. This program involves determination of the properties of all of the more-important sulfur-containing compounds that occur naturally in petroleum. It is necessary to know the properties of these substances in order to remove those that are injurious and to isolate and process those that are finding useful applications in industry. The long-range program of investigation of the properties of hydrocarbons also has continued with unabated vigor and many important results have been obtained. The various types of investigation that are carried out in the Bureau of Mines laboratories are: (1) Low-temperature calorimetry; (2) heats-of-combustion studies; (3) vapor-heat capacity and heats-of-vaporization measurements; (4) vapor-pressure determinations; and (5) the calculation of thermodynamic properties by statistical mechanics. Progress in these five fields of investigation are described in the sections that follow.

57/ Holliman, W. C., Useful Products from Natural Gas: Conference on Gas Technology, Texas School of Arts and Industries, Kingsville, Tex., May 30, 1951.

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Low-Temperature Calorimetry

To make positive predictions of the feasibility of a proposed large-scale chemical process, it is necessary to know the value of the thermodynamic property called the entropy for each of the chemical substances involved. The entropy may be computed from knowledge of the low-temperature heat capacity, heats of transition, heats of fusion, and melting points of the substance of interest. Using liquid hydrogen and liquid air as coolants, the entropy of a number of compounds has been measured during the past year over the temperature range -440° F. to room temperature.

One of the leading aviation laboratories became interested in a special hydrocarbon fuel named spiropentane. The low-temperature properties of this substance have been measured, and the results have been published in the Journal of the American Chemical Society.[58] Studies also were conducted on a related pair of hydrocarbon molecules of great industrial importance. These two substances are 2-methylbutane (isopentane) and 2,3-dimethylbutane (diisopropyl). The results of this investigation were published in the same journal.[59] The results of studies at low temperatures on 2-thiabutane (methyl-ethyl sulfide) have been published also.[60] The sulfur compounds 2-methyl-2-propanethiol,[61] thiacyclopropane and 2-propanethiol[62] have been investigated and the results reported to the American Petroleum Institute for immediate distribution to approximately 150 research organizations. In addition, a number of hydrocarbon molecules, a part of the long-range hydrocarbon program, have been studied, and the results have been transmitted to the American Petroleum Institute Research Project 44 for use in a complete revision of the calculated values of the thermodynamic properties of the entire known body of hydrocarbons.

Vapor-Heat Capacity and Heat of Vaporization

In order to extend the range of usefulness of low-temperature data, it is necessary to measure the heat capacity of hydrocarbon gases and to determine the heat of vaporization of the compound of interest. Therefore, when the chemical stability of the compound of interest permits, the two aforementioned properties are measured.

During the study of some of the most corrosive types of sulfur compounds, severe problems were encountered that necessitated the development of corrosion-proof

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58/ Scott, D. W., Finke, H. L., Hubbard, W. N., McCullough, J. P., Gross, M. E., Williamson, K. D., Waddington, Guy, and Huffman, H. M., Spiropentane: Heat Capacity, Heats of Fusion and Vaporization, Vapor Pressure, Entropy and Thermodynamic Functions: Jour. Am. Chem. Soc., vol. 72, 1950, p. 4664.

59/ Scott, D W., McCullough, J. P., Williamson, K. D., and Waddington, Guy, Rotational Isomerism and Thermodynamic Functions of 2-Methylbutane and 2,3-Dimethylbutane. Vapor Heat Capacity and Heat of Vaporization of 2-Methylbutane: Jour. Am. Chem. Soc., vol. 73, 1951, p. 1707.

60/ Scott, D. W., Finke, H. L., McCullough, J. P., Gross, M. E., Williamson, K. D., Waddington, Guy, and Huffman, H. M., Thermodynamic Properties and Rotational Isomerism of 2-Thiabutane: Jour. Am. Chem. Soc., vol. 73, 1951, p. 261.

61/ American Petroleum Institute, Research Project 48A Annual Report: No. 3, Oct. 1, 1949, to Oct. 1, 1950.

62/ American Petroleum Institute, Research Project 48A Quarterly Report: No. 8, Apr. 1, 1951 to July 1, 1951.

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apparatus. The new apparatus was successfully applied to determination of the properties of 2-propanethiol,[63] thiacyclopentane,[64] and 3,4-dithiahexane.[65] It should be pointed out that the data mentioned in this and the previous section permit an evaluation of certain facts concerning the shape and behavior of molecules. This knowledge of molecular structure is of great interest to fundamental research workers and finds application in the developing science of petroleum chemistry.

Combustion Calorimetry

A knowledge of the heat of combustion of a given reaction is extremely important in designing equipment and in finding the proper operating conditions for industrial processes. Methods for determining the heat of combustion of hydrocarbons have been improved until this is one of the most accurate of all measurements. However, methods for carrying out similar investigations on compounds containing sulfur, chlorine, and other atoms that yield corrosive products are lacking. For this reason, the Bureau of Mines for several years has been making a determined effort to find experimental methods that will provide accurate values of the heat of combustion of organosulfur compounds. During the past year the methods have been improved to an extent that the problem may be regarded as largely solved. A preliminary account of this work has been prepared for publication.[66] The success of this development has come at a time when it may be applied immediately to defense problems of pressing nature. This phase of the thermodynamic work undoubtedly will produce a large amount of useful information within the next few years. Successful measurements have been carried out on elemental sulfur and pentanethiol.[67]

Vapor Pressure

To describe properly the behavior of a hydrocarbon or hydrocarbon derivative in the temperature region where liquid and vapor may coexist, it is necessary to have a knowledge of the vapor pressure of the substance. This laboratory has two types of equipment with which vapor pressure may be measured in the low-pressure and moderate-pressure regions. During 1951 these methods have been applied to give accurate values of the vapor pressures of 2-propanethiol,[68] thiacyclobutane,[69] thiacyclopentane,[70] 3,4-dithiahexane,[71] and thiacyclopropane[72] as a part of the program of American Petroleum Institute Research Project 48A. Thiacyclopropane is so unstable chemically that initially it was thought impractical to carry out vapor-pressure measurements on it. However, special techniques were devised, and the results obtained were entirely satisfactory. In addition to the measurements carried out on sulfur compounds, similar studies were made on tetramethylethylene and tetrahydrofuran, two compounds of considerable industrial importance and fundamental scientific interest.

63/ See footnote 60.
64/ American Petroleum Institute, Research Project 48A Quarterly Report: No. 7, Jan. 1, 1951, to Apr. 1, 1951.
65/ See footnote 62.
66/ Hubbard, Ward N., and Waddington, Guy, A Report for the Commission on Thermochemistry of the International Union of Pure and Applied Chemistry on Reactions Involving Combustion in a Bomb of Compounds Containing Sulfur: Thermodynamics Laboratory, Bureau of Mines, Bartlesville, Okla.
67/ See footnote 64.
68/ See footnote 62.
69/ See footnote 62.
70/ See footnote 64.
71/ See footnote 62.
72/ See footnote 62.

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Statistical Mechanical Calculations

The experimental investigations described give thermodynamic properties in the temperature range -440° F. to approximately +400° F. These data are directly applicable to many practical problems, but many other industrial reactions are carried out at temperatures above those at which laboratory measurements are feasible. Fortunately, the methods of theoretical chemistry permit the calculation of required thermodynamic properties at high temperatures. The facts on which the theoretical calculations are based are spectroscopic data, the distances and angles between the atoms of the molecule in question, and certain of the measured values described in the foregoing sections. Using these methods, high-temperature thermodynamic data have been obtained for the sulfur compounds, 2-thiabutane,[73] and ethylmercaptan.[74] Similar computations for thiacyclopropane, 3,4-dithiahexane, 3-thiapentane, and 2-methyl-2-propanethiol are nearly complete.

TRANSPORTATION OF NATURAL GAS

Three important phases of research in the field of natural-gas production, transportation, and processing are conducted in cooperation with the American Gas Association at the Amarillo Helium Plant, Amarillo, Tex. This research includes: (1) The problem of removal of excess nitrogen from the gas; (2) development of a dew-point recorder to improve plant and pipeline operation; and (3) study of flow of gas in pipelines.

Removal of Excess Nitrogen from Natural Gas

Changing economic conditions limited interest in the problem of removing nitrogen from natural gas to the review of past experimentation and preparation of results in publication form. A critical survey of experimental work indicates that adsorption and low-temperature processing are the methods that show most promise for economical removal of nitrogen from natural gas. By using these methods, nitrogen may be removed at a cost slightly more than savings made by increased pipeline deliverability. Further gain in economic advantage may result from coincidental dehydration of the gas, increased L.P.G. recovery, and, in some instances, greatly improved marketability.

Dew-Point Recorder for Natural Gas

Movement of natural gas from areas where it is produced and its delivery to and from distribution lines and processing plants require accurate knowledge of the component parts of the gas. One of the important determinations of composition is the water-vapor content. The sale of natural gas is subject to contract commitments that limit the amount of water vapor that may be present. To assure a maintained minimum quantity of water vapor, constant analysis of delivered gas is necessary. The water-vapor recorder developed by the Bureau in cooperation with the American Gas Association lends itself well to checks on water-vapor content and as a control device to assure constant adjustment of plant-dehydration equipment, which keeps water vapor to a required minimum.

Extensive tests have proved that, when activated alumina is used to remove water vapor from the flowing natural gas, it offers no interference in dew-point

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73/ See footnote 60.
74/ American Petroleum Institute, Research Project 48A Annual Report: No. 3, Oct. 1, 1949, to Oct. 1, 1950.

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measurements. Similarly, when diethylene glycol is used to remove water vapor, the dew-point recorder operates successfully, when adapted, by using a suitable filter to remove traces of the dehydrator.

To remove acid gases from the flowing stream it is usually treated with monoethanolamine, which interferes with dew-point measurements. To minimize the effect of amine vapors, the sample stream was treated with oxalic acid, which combined with amine to form a reaction product that was a white solid, which could be kept from the hygrometer by means of a suitable filter. Constant improvement of the water-vapor recorder has made it suitable for wider use throughout the natural-gas industry. An article describing the instrument is being prepared for publication.

Flow of Natural Gas in Pipelines

In recent years it has become increasingly evident that more factual information was needed to predict line pressures and flow capacities successfully, particularly when operational conditions necessitated the construction of larger-diameter pipelines containing natural gas at higher pressures than was common during the early development of flow formulas. A most-important factor, when considering flow in both horizontal and vertical tubes, is the relative roughness of the inside wall of the tube. Recognizing the importance of bringing up to date the methods of computing the flow capacity of new, as well as old, lines, the Bureau (in cooperation with the American Gas Association) has continued to work on this important problem.

To supplement data already obtained, seven experimental pipelines were tested, ranging in size from 2- to 8 inches and with various surface conditions representing mirror-finish, stainless-steel, welded, and seamless-steel pipes. These tests, conducted under a cooperative agreement with Pacific Lighting Gas Supply Co., were made at Goleta, Calif., where favorable conditions existed. During this work, special high-pressure manometers were developed that made possible simultaneous recording of differential pressures needed in the tests. Through the cooperation of the College Park and Pittsburgh Stations of the Bureau of Mines, arrangements have been made to correlate and analyze the experimental data by use of punched-card electronic calculators.

HELIUM-TRACER STUDIES

Personnel of the Amarillo, Tex., helium plant were assigned the problem of investigating the use of helium as a tracer gas in petroleum reservoirs and carried the development to completion. The results obtained continue to be of great interest to the petroleum industry, as evidenced by continued requests for information and assistance. Consulting and field-engineering assistance was given in beginning three helium-tracer-gas projects, two in Texas and one in California, and preliminary information and engineering recommendations were given on projects in several additional fields during the year. In one of the projects on which assistance was given, the tracer helium appeared within approximately 24 hours in the gas produced from wells adjacent to the injection wells and thus answered the principal question as to whether the wells produced from the same reservoir as the injection well. In another instance, in which a barrier was presumed to exist between the injection well and a producing well under test, the tracer gas appeared in the gas produced from the latter approximately 8 days after beginning the addition of tracer gas, and this disproved the presence of the barrier.

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A report[75] covering work done on a cooperative helium-tracer-gas project in West Virginia was published previously. An article[76] giving results of tests using helium as a tracer gas in a field in Arkansas also has been published.

EFFECTS OF PROGRAM

Each line of endeavor within the petroleum and natural-gas program of the Bureau has been programed to possible demands of a national emergency. Each major project is ready to supply information, technical assistance, and service to Government and industry in the problems of defense preparation. The primary-production program has as its objective conservation and efficient use of the natural energy inherent in most oil and gas reservoirs. The secondary-recovery work is concerned with stimulating production in the partly depleted fields by replacing the energy needed to increase ultimate recovery. These are long-range endeavors to which may be added a recent special assignment for the Petroleum Administration for Defense. Close cooperation between major projects gave the needed results without undue interference with normal peacetime research.

The chemistry and refining and the thermodynamics groups furnished basic scientific facts that will allow industry to make more and better products at lower cost through conservation of materials in the design of new and the improvement of old processes. A recent correlation based on crude-oil analyses, obtained over a period of many years, will furnish refiners needed information quickly and eliminate time-consuming experimentation.

The Bureau's program of research on problems of natural-gas transportation furnished the industry with new engineering techniques and methods for eliminating technical difficulties experienced in producing and transporting natural gas. Detection and removal of undesirable materials from the gas will save the cost that would be incurred in transporting the undesirable components of the fuel to widely scattered areas.

The research and engineering studies of the Bureau's program in the field of petroleum and natural gas, in close cooperation with industry, will help to increase the quantity, quality, and - of importance in time of national emergency - availability of petroleum products. Constant exchange of ideas in the scientific field between scientists from other nations will create immediate and future good relationship among all concerned.

75/ Frost, E. M., Jr., Helium Tracer-Gas Studies in the Cabin Creek, W. Va., Oil and Gas Field: Bureau of Mines Rept. of Investigations 4715, 1950, 28 pp.

76/ Frost, E. M., Jr., Helium Tracer Studies in the Shuler Arkansas Field: Petrol. Eng., March 1951, vol. 23, No. 3, pp. B-7 to B-12, B-16, B-18, and B-20.

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